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THE BEHAVIOUR OF THE FLUORITE MEMBRANE ELECTRODE IN SOLUTIONS OF MAGNESIUM SALTS

by

M. MROST and R. ARNOLD

OPSOMMING

Florietmembraan—elektrodes is gemaak en die e.m.k. oor die membraan is in die teenwoordigheid van verskillende soute bepaal. In elke geval was die konsentrasies van die toetssout verskillend aan verskillende kante van die membraan. Omkeerbare en reproduseerbare potensiale is gemeet in die geval van oplossings van magnesium sowel as kalsiumsoute. Hierdie potensiale volg die Nernst-vergelyking.

Die chloriede, nitrate, sulfate en asetate van hierdie metale het dieselfde resultaat gelewer; kaliumchloried in die oplossing verslaag egter die e.m.k.-waardes. Dit is bevind dat fluorietmembrane 'n klein asimmetriepotensiaal in oplossings van kalsium- en magnesiumsoute gee.

Die gedrag van fluorietmembraan in oplossings van kalium-, natrium-, ammonium-, lood- en aluminiumchloriede is ook ondersoek. In hierdie gevalle was daar geen e.m.k. oor die membraan nie.

Daar moet verdere ondersoek ingestel word na sekere verskynsels soos byv. nul-e.m.k.'s.

SUMMARY

Fluorite membrane electrodes have been constructed and the e.m.f. across the membrane has been measured in the presence of various salts; in each case the concentration of the salt under investigation being different on each side of the membrane. Reversible and reproducible potentials were obtained not only in calcium salt solutions, but also in solutions of magnesium salts. These potentials are in accordance with the Nernst equation.

The chlorides, nitrates, sulphates and acetates of these metals gave identical results; the presence of potassium chloride in the solution, however, lowered the e.m.f. values. It has been found that fluorite membranes display a small asymetry potential in solutions of calcium and magnesium salts.

The behaviour of fluorite membranes has also been investigated in solutions of potassium, sodium, ammonium, lead and aluminium chlorides. In these cases the e.m.f. across the membrane was found to be zero.

Further work is required to explain certain observations, especially that of zero e.m.f.

Fluorite membrane electrodes were successfully used to determine calcium ion concentrations in milk and in gum arabic solutions by Tendeloo.[1] However, this author gives no mechanism for the behaviour of fluorite membranes, apart from suggesting that cation exchange occurs between the membrane and the external solution. The theoretical treatment of membrane behaviour proposed by Teorell[2] and developed by Meyer and Sievers,[3] and later by Marshall and his co-workers,[4] refers primarily to ion-selective membranes prepared from materials in which the cation is loosely bonded to an anion of colloidal dimensions. Fluorite differs markedly in structure from such materials.

The present work arose out of an attempt to develop an electrometric method for estimating magnesium in dilute solution. It has been shown that the calcium fluoride membrane electrode is sensitive to magnesium ions, but behaves in an anomalous manner when other ions are present. Furthermore, the applicability of existing theories of membrane electrodes to this system has been considered.

EXPERIMENTAL

Preparation of membranes

Tendeloo, in his published work, gives no details of the method he used for grinding fluorite crystals to thin membranes. The method employed here involves the use of a rotating grinding plate. Three retaining screws hold a glass plate against a brass wheel

mounted on the spindle of a small electric motor. A ring of rubber tubing between the glass plate and the brass wheel allows of accurate adjustment of the plate in a plane perpendicular to the axis of the motor spindle. A clear, flawless crystal of fluorite, mounted on a thickened glass tube with Canada balsam, can then be brought to bear on the glass plate. The glass tube is held in the trough formed between two horizontal glass rods mounted on the same board as the motor, thus fixing its position with respect to the glass grinding plate. A plane surface may thus be ground on the crystal. The abrasive employed was —600 mesh aluminium oxide.

When one plane face has been ground on the crystal, it is removed from the glass tube, turned, and cemented to the same glass tube with sealing wax. A second plane surface, parallel with the first, is then ground on the crystal. The final thickness of the crystal is between 0·08 and 0·1 mm.

The exposed sealing wax surface surrounding the mounted crystal is covered with a layer of paraffin wax to ensure the maintenance of insulated and leak-proof conditions at the crystal edges.

Checking of membranes for cracks and leaks

Anderson[5] has suggested that the e.m.f. values obtained with fluorite membranes may be due to junction potentials established in cracks in the fluorite crystals, and that the crystals therefore function as "crack" electrodes. The following experiments, therefore, were performed in order to ensure that no cracks were present in the crystals:

(i) The mounted membranes were individually tested for porosity, before use, by immersing the open ends of the supporting tubes in water. Any decrease in volume of the air thus trapped and compressed within the tube would indicate that air had been forced through the membrane. Several such membranes were found and discarded. In a few instances the tubes were inverted over mercury and a quantity of hydrogen or carbon dioxide introduced into the upper part of the tube.

All the crystals used were thus tested for impermeability to gases for a period of not less than forty-eight hours. The head of water used was not less than 6·0 cm., and the head of mercury not less than 0·5 cm. Having thus ensured that the membranes are impervious to gases, even to hydrogen, it was concluded that no mechanical penetration of liquid through the membrane would take place.

(ii) Several membranes were removed from their tubes when they had been in service for some time, and soaked in a solution of methylene blue. Subsequent examination of the membranes under the microscope failed to reveal the presence of any cracks, the existence of which would have been shown by the retention of the dyestuff in such cracks.

Reference electrodes

Silver-silver chloride electrodes were prepared by the usual method of depositing silver on a platinum wire from a solution of potassium argento-cyanide and anodically chloridizing in a solution of hydrochloric acid.

The calomel electrodes employed were standardized against quinhydrone electrodes in known buffer solutions. Where pairs of calomel electrodes were used in one cell, these electrodes were standardized against each other. Only those electrode pairs which were within 0·5 mv. of each other were employed.

Cell arrangements employed

The cell arrangements employed were as follows:—

(i) Ag | AgCl | xM — $CaCl_2$ || Membrane || yM — $CaCl_2$ or $MgCl_2$ | Saturated KCl | Calomel electrode

(ii) Calomel electrode | saturated KCl | xM — $MgCl_2$ | Membrane | yM — $CaCl_2$ or $MgCl_2$ | Saturated KCl | Calomel electrode

The first arrangement is similar to that employed by Tendeloo, while the second is similar to that employed by Marshall. Cells of the second type give rise to rather small electromotive force values. In some instances, therefore, a Weston cell was connected in series witn the experimental cell so that measurements could be made away from the end of the potentiometer slide wire.

Measurements of electromotive force were carried out by means of a Cambridge electrometer valve potentiometer.

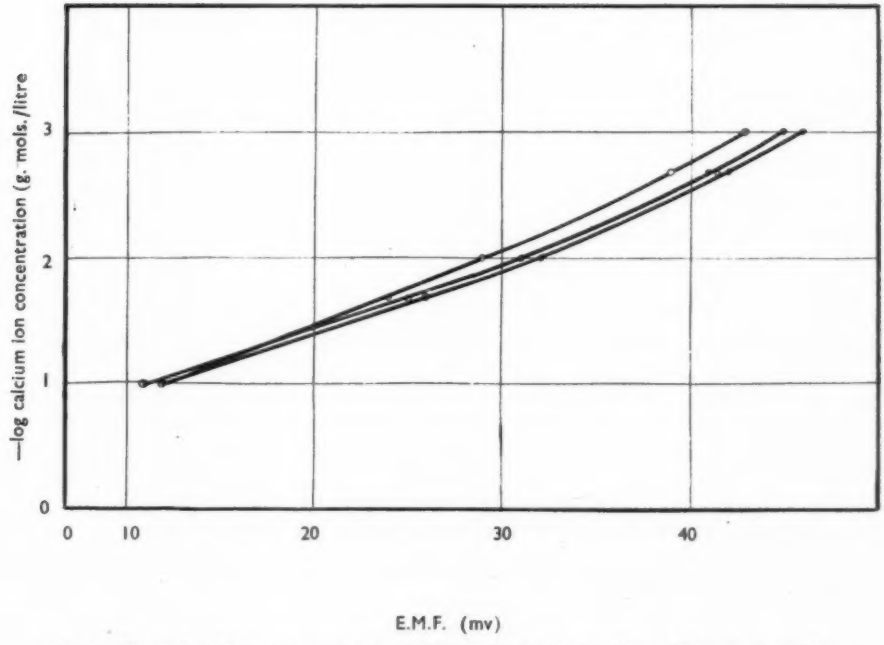

Fig. 1. Effect of calcium concentration on E.M.F. obtained with three different electrodes.

TABLE I

Electrode No.	*$CaCl_2$ Molarity*	*e.m.f. (milli-volts)*	*e.m.f. Difference (milli-volts)*	*Corresponding values obtained by Tendeloo*	
				e.m.f. (milli-volts)	*e.m.f. Difference (milli-volts)*
1	0·1	4		— 54·5	
			4		13·5
	0·05	8			
			10	— 41·0	
	0·01	18			
			6		27·5
	0·005	24			
			14	— 13·5	
	0·001	38			
			(16)		
	0·0001	(54)			
2	0·1	7			
			4		
	0·05	11			
			10		
	0·01	21			
			5		
	0·005	26			
			12		
	0·001	38			
			(12)		
	0·0001	(50)			
4	0·1	5			
			4		
	0·05	9			
			10		
	0·0f	19			
			6		
	0·005	25			
			14		
	0·001	39			
			(17)		
	0·0001	(56)			

Note:—
(i) The 0·5 M — $CaCl_2$ solution constitutes the positive side of the membrane.
(ii) Electrodes 3 and 5 yielded somewhat erratic values due to the crystals being too thick and their resistance consequently too high for satisfactory measurements to be possible on the potentiometer.
(iii) Values of the e.m.f. obtained in 0·0001 M. solutions were subject to drifting and are doubtful.

RESULTS

The behaviour of fluorite membranes in solutions of calcium chloride

Five membranes were prepared by the method previously outlined, and included in the following cell arrangement:—

Ag | AgCl | 0·5M — $CaCl_2$ | Membrane | xM — $CaCl_2$ | saturated KCl | Calomel electrode

where x = 0·1, 0·05, 0·01, 0·005, 0·001 or 0·0001.

The silver-silver chloride electrode and the 0·5M—$CaCl_2$ were contained inside the glass tube on which the membrane had been sealed. The calcium chloride solutions employed were prepared by accurate dilution of the 0·1 M. solution.

The results obtained are recorded in Table I together with some of the results obtained by Tendeloo. It will be noted that the ratio of successive concentrations of calcium chloride is alternately 2 and 5; hence the alternating nature of the e.m.f. differences.

These results appear to be substantially in agreement with those of Tendeloo, especially in so far as the differences in the e.m.f. obtained with the membrane in solutions of different concentrations are concerned. The differences in the absolute values are due in part to the fact that Tendeloo used a normal calomel electrode whereas a saturated calomel electrode was used in the above determinations.

In the graphical representation of these values (Fig. 1) -log [Ca++] is plotted against e.m.f. and a graph is obtained which approximates to the straight line relationship predicted by the Nernst equation, namely, that E is a linear function of log a_1/a_2; however, since concentrations are used here in place of activities, it is to be expected that the Nernst relation is not followed accurately.

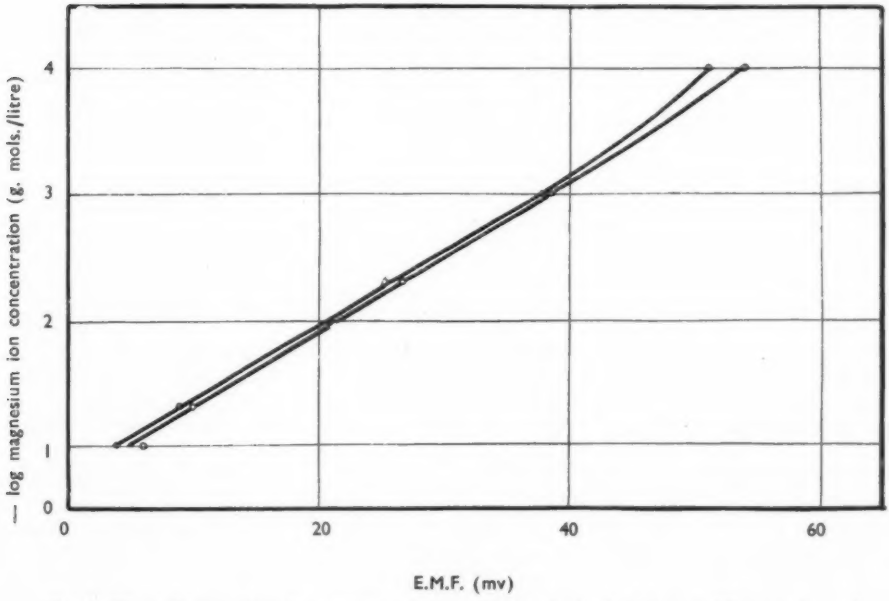

Fig. 2. Effect of magnesinm ion concentration on E.M.F. obtained with two different electrodes.

The behavior of flourite membranes in solutions of magnesium chloride

Electrodes 1, 2 and 4 were included in the following cell arrangement:—

Ag | AgCl | 0·5M — $CaCl_2$ | Membrane | xM — $MgCl_2$ | Saturated KCl | Calomel electrode

where x = 0·1, 0·05, 0·01, 0·005, 0·001 or 0·0001.

The silver-silver chloride electrode and the 0·5M—$CaCl_2$ were contained in the glass tube on which the membrane had been sealed. The magnesium chloride solutions employed were prepared by accurate dilution of the 0·1 M. solution.

The e.m.f. values obtained with the flourite membrane assemblies 1, 2 and 4 are shown in Table II.

TABLE II

Electrode No.	*$MgCl_2$ Molarity*	*e.m.f. of cell (milli-volts)*				*e.m.f. Difference (mv.)*
		1	2	3	*Mean*	
1	0·1	4·0	4·5	4·0	4·0	
						5·0
	0·05	9·0	9·0	10·0	9·0	
						12·0
	0·01	21·0	21·5	20·5	21·0	
						5·0
	0·005	25·0	26·0	26·0	26·0	
						12·0
	0·001	38·0	38·0	38·0	38·0	
						13·0
	0·0001	50·0	51·5	51·5	51·0	
2	0·1	6·0	6·0	6·0	6·0	
						4·0
	0·05	10·5	10·0	10·0	10·0	
						11·0
	0·01	21·0	21·0	21·0	21·0	
						5·5
	0·005	27·5	26·0	26·0	26·5	
						12·0
	0·001	38·0	39·0	39·0	38·5	
						15·5
	0·0001	57·0	49·0	49·0	54·0	
4	0·1	5·0	5·0	5·0	5·0	
						4·0
	0·05	8·0	9·5	9·5	9·0	
						12·0
	0·01	20·5	20·0	22·0	21·0	
						4·5
	0·005	25·0	25·5	25·5	25·5	
						13·5
	0·001	38·0	39·0	39·0	39·0	
						20·0
	0·0001	56·0	63·0	58·0	59·0	

Note:—Columns 1–3 refer to three separate determinations.

(i) The 0·5 M — $CaCl_2$ solution constituted the positive side of the cell.

(ii) The values obtained in solutions of 0·0001 M — $MgCl_2$ were stable and not subject to the drifting of e.m.f. observed in $CaCl_2$ solutions.

During this series of determinations the electrodes were stored in distilled water, no special precautions for their preservation having been found necessary. The 0·5 M—$CaCl_2$ solutions contained within the tube on which the membrane was mounted was changed only when the formation of a fine white precipitate on the surface of the solution was observed. The precipitate probably consisted of calcium carbonate.

These results are shown graphically in Fig. 2 from which it will be seen that an even closer approximation to the Nernst equation is obtained than in the case of calcium ions. It is thus evident that the calcium fluoride membrane electrodes respond to magnesium in the same way as to calcium.

The influence of anions on the membrane potentials

Solutions of magnesium nitrate, magnesium sulphate and magnesium acetate were prepared as representative of solutions of magnesium salts of monobasic, dibasic and organic acids.

Five more electrodes were prepared and checked for uniform behaviour against solutions of magnesium chloride, and, as before, they were checked for possible leaks by inversion of the tubes over water.

Membranes 2, 6 and 8 were selected for the following experiments.

The cell arrangements employed were:—

Ag | AgCl	0·5M — $CaCl_2$	Membrane	xM — $Mg(NO_3)_2$ or xM — $Mg(CH_3COO)_2$ or xM — $MgSO_4$	Saturated KCl	Calomel electrode

where x = 0·1, 0·05, 0·01, 0·005 or 0·001.

The e.m.f values obtained are shown in Table III.

From Table III it will be observed that:—

(i) The e.m.f increases for corresponding increases in magnesium ion concentration are substantially the same whether the magnesium salt used is the nitrate, sulphate or acetate. These values are, further, in agreement with those found for magnesium chloride.

(ii) The potentials for Membrane No. 6 are generally higher than those obtained with other electrodes and in general slight differences in e.m.f. are observed for the same solutions with different membranes.

Since the Ag | AgC1 electrodes balanced each other exactly, and further, since the same calomel electrode was used throughout the above series of determinations, it would appear from the variation in absolute e.m.f. values found with different membranes that the membrane may set up an asymmetry potential.

This was examined as described in the following section.

The determination of the asymmetry potential of fluorite membranes

The procedure adopted was as follows:— The membrane was set up with the same concentration of megnesium chloride on each side, and calomel electrodes, which had been standardized against each other, as reference electrodes on each side. Thus, where the calomel electrodes balance each other and the membrane asymmetry potential is zero, the cell should have a zero e.m.f.

Determinations were carried out at two magnesium chloride concentrations, i.e., 0·1 M. and 0·001 M.

The cell assembly, therefore, was:—

Calomel electrode	Saturated KCl	xM — $MgCl_2$	Membrane	xM—$MgCl_2$	Saturated KCl	Calomel electrode

where x = 0·1 or 0·001.

TABLE III

Electrode No.	*Solution*	$Mg(NO_3)_2$		$MgSO_4$		$Mg(CH_3COO)_2$	
	Molarity	*e.m.f. (mv.)*	*Increase (mv.)*	*e.m.f. (mv.)*	*Increase (mv.)*	*e.m.f. (mv.)*	*Increase (mv.)*
2	0·1	5·0		4·5		4·5	
			6·0		6·5		5·5
	0·05	11·0		11·0		10·0	
			10·0		9·5		10·5
	0·01	21·0		20·5		20·5	
			5·0		6·0		5·5
	0·005	26·5		26·4		26·0	
			11·5		11·0		11·5
	0·001	38·0		37·5		37·5	
6	0·1	9·0		9·0		8·5	
			4·0		4·5		4·5
	0·05	13·0		13·5		13·0	
			11·0		10·5		10·0
	0·01	24·0		24·0		23·0	
			4·5		4·5		5·0
	0·005	28·5		28·5		28·0	
			11·0		10·5		11·0
	0·001	39·5		39·0		39·0	
8	0·1	5·5		6·0		5·5	
			5·5		5·5		5·5
	0·05	11·0		11·5		11·0	
			11·0		10·5		10·0
	0·01	22·0		22·0		21·0	
			5·0		5·0		5·5
	0·005	27·0		27·0		26·5	
			11·0		12·0		11·0
	0·001	38·0		39·0		37·5	

TABLE IV

Electrode No.	*Asymmetry potential (mv)*	
	in $0{\cdot}1M - MgCl_2$	*in* $0{\cdot}001M - MgCl_2$
1	−0·25	0
2	0	0
4	0	−0·25
6	+3·25	+2·75
7	+1·25	0
8	+0·25	+0·25
9	0	−0·25
10	+0·75	+1·25

A standard Weston cell was included in the external circuit in order to obviate the use of the extreme end of the potentionmeter wire. For each determination two readings were taken, one with the membrane cell and the Weston cell in series and one with the two cells in opposition. The membrane cell potential is thus equal to half the difference of the two readings and is independent of the e.m.f. of the Weston cell. It was found that

the two calomel electrodes used differed in potential by 0·25 mv., that serving as inner reference electrode having the higher potential. The observed values, therefore, were corrected by subtracting 0·25 mv. to give the final asymmetry potential.

The observations and asymmetry potential of several membranes in solutions of 0·1 M. and 0·001 M—$MgCl_2$ are shown in Table IV.

On the basis of these results membranes Nos. 1, 2, 4, 8 and 9 were selected for future use since they displayed an asymmetry potential of less than 1 milli-volt which varied by less than 0·25 milli-volts between 0·1 M—$MgCl_2$ and 0·001M—$MgCl_2$ solutions.

These results explain the rather high values obtained with membrane No. 6 as shown in Table III.

The behaviour of fluorite membranes in magnesium chloride solutions of known activity

Clearly, it would be desirable to compare the potentials obtained with those predicted by the Nernst equation in the form $E = (RT/nF)\ 1n\ a_1/a_2$ where a_1 and a_2 refer to ion activities on each side of the membrane. This comparison requires a knowledge of magnesium ion activities.

Therefore, it was decided to estimate magnesium ion activities by a method which was used by Marshall.

The method is developed as follows:—
For any given value of the ionic strength it is assumed that the activity of the chloride ion is the same in solutions of magnesium, calcium or potassium chloride. Further, it is assumed that in solutions of potassium chloride the potassium and chloride ions have the same activity. On the basis of these assumptions, and employing values for the activity coefficients of $MgCl_2$ and KCl obtained from the literature, a series of $MgCl_2$ solutions of magnesium ion activity 0·001, 0·003, 0·009, 0·027, 0·081 and 0·243, was prepared. A constant e.m.f. difference of 0 ·0138 volts between consecutive solutions separated by a membrane, could thus be anticipated if the membrane behaved reversibly in accordance with the Nernst equation.

The estimation of single ion activities by this method is, of course, not theoretically correct, although it is sometimes empirically useful.[6] It appeared subsequently (see Discussion) that we can in any case not be certain that it is the magnesium ion, rather than the anion, which is responsible for the establishment of the potential difference. Use of the activity coefficients of magnesium chloride, however, rather than those calculated above, alters the value of the theoretical electromotive force by less than the experimental error, and the data, therefore, have been left in the present form.

e.m.f. of cells of the type

Calomel electrode	Saturated KCl	$a^{I}_{MgCl_2}$	Membrane	$a^{II}_{MgCl_2}$	Saturated KCl	Calomel electrode

The arrangement used to this stage had been that of Tendeloo, where a silver-silver chloride electrode dipped directly into the inner solution of the membrane electrode. This arrangement served to confirm Tendeloo's work and to show that the membrane electrode functions in the same manner in magnesium solutions. However, it would not be suitable here for the following reasons. If equilibrium is established between the inner surface of the membrane and the solution, the chloride ions in the solution will be at the same chemical potential as at the membrane surface, and since the potential of the

silver-silver chloride electrode depends on the chemical potentials of the chloride ions, the potential difference between the latter electrode and the membrane will be independent of the concentration of the inner solution. Therefore, we measure only variations in the activity of the outer solution. It was now desired to study the effect on the e.m.f. of the cell of the ratio of concentrations in the outer and inner solutions. Thus it was necessary to separate the reference electrodes from these solutions by means of salt bridges.

The calomel reference electrodes used in these cells balanced each other. The ratio of the magnesium activities of the solutions used was 3.

The results obtained with membranes 1, 2 and 8 are shown in Table V. In Fig. 3 the e.m.f. values of the cells are plotted against the log of the activity of the more dilute solution.

TABLE V

Membrane	*Mg ion activity (inside tube)*	*Mg ion activity (outside tube)*	*Cell e.m.f. (milli-volts)*			
			1	2	3	*Mean*
1	0·243	0·081	6·5	6·5	7·5	7·0
	0·081	0·027	13·5	13·0	13·5	13·2
	0·027	0·009	13·5	13·8	13·2	13·5
	0·009	0·003	13·8	13·8	13·5	13·7
	0·003	0·001	13·7	13·6	13·9	13·7
2	0·243	0·081	12·0	12·0	12·2	12·0
	0·081	0·027	14·3	14·5	13·5	14·1
	0·027	0·009	14·2	14·2	14·0	14·1
	0·009	0·003	14·6	14·0	14·0	14·2
	0·003	0·001	14·2	14·2	14·3	14·2
8	0·243	0·081	8·0	9·5	9·5	9·0
	0·081	0·027	13·2	13·5	12·2	12·8
	0·027	0·009	13·5	13·3	12·0	13·0
	0·009	0·003	13·2	13·4	13·0	13·2
	0·003	0·001	13·5	13·0	13·0	13·2

Note.—Columns 1–3 in Table V refer to three separate determinations.

It will be seen that between the values of 0·1 and 0·001 magnesium ion activity the e.m.f. differences remain reasonably constant and agree substantially with the value of 13·8 milli-volts which, according to the Nernst theory, should be produced by a reversible electrode.

Note: (i) When the solution of 0·001 activity was diluted threefold and employed on one side of the membrane, e.m.f. values were obtained which, though constant during individual measurements, were not reproducible. Therefore, it would appear that the electrode is not applicable to such low magnesium ion activities.

(ii) In the above series of measurements the more concentrated solution was always on the positive side of the cell.

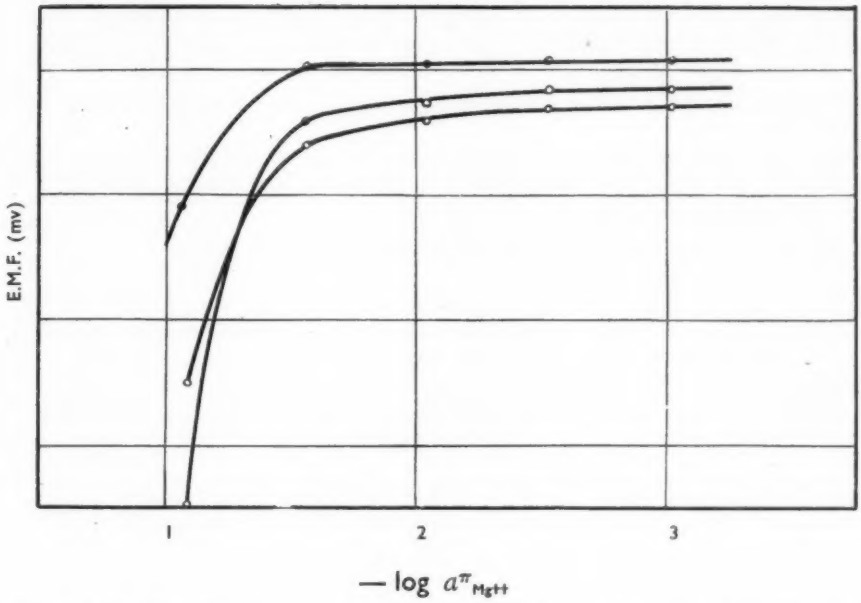

Fig. 3. Variation of e.m.f. of fluorite membrane electrodes with magnesium ion activity. The ratio of the activities on each side of the membrane was always 3; plotted above is the log of the activity in the more dilute solution.

The effect of cations other than calcium and magnesium

The effect of solutions of KCl, NaCl, NH_4Cl, $PbCl_2$ and $AlCl_3$ were studied. Lead was chosen as the divalent cation since it was felt that the membrane might be selective towards cations forming insoluble fluorides. 0·1 M. and 0·001 M. solutions of these salts were prepared and included in the following cell arrangement:—

Calomel electrode	Saturated KCl	0·1M. solution	Membrane	0·001 M. solution	Saturated KCl	Calomel electrode

In no instance was any measurable potential produced across the membrane.

The determinations were made more sensitive by the inclusion of a Weston cell in the cell assembly and obtaining two readings of the potential with the Weston cell first connected to the dilute solution of the membrane cell, and then to the concentrated solution. The values obtained, however, were always the same and agreed with the e.m.f. of the Weston cell.

The behaviour of the electrodes in the presence of both potassium and magnesium ions

The purpose of this experiment was to determine whether or not the sensitivity of the fluorite membrane to solutions of calcium and magnesium salts is interfered with by the presence of potassium chloride, which, from previous experiments, appears not to affect the membrane.

Potassium chloride solutions were prepared having activities of 0·0009, 0·0027 and 0·0081 respectively.

The magnesium chloride solutions in which the membranes were immersed were prepared by the dilution of the previously used solutions of known activity with:—

(i) an equal volume of water, and

(ii) an equal volume of a potassium chloride solution of known activity.

TABLE VI

Inside membrane tube		*Outside membrane tube*	*e.m.f. of cell (millivolts)*	*Differences in e.m.f. (millivolts)*
*Mg^{++} and K^{+} activities of the solutions from which the test solution was prepared.**		*Mg^{++} activities of the solutions before dilution with an equal volume of water*		
$a_{Mg^{++}}$	*$a_{K^{+}}$*	*$a_{Mg^{++}}$*		
0·243	0·0081	0·081	6·0	
				8·0
		0·027	14·0	
				8·0
		0·009	22·0	
				8·0
		0·003	30·0	
				4·0
		0·001	34·0	
0·243	0·0027	0·081	7·0	
				10·0
		0·027	17·0	
				10·0
		0·009	27·0	
				8·0
		0·003	35·0	
				6·0
		0·001	41·0	
0·243	0·0009	0·081	7·0	
				12·5
		0·027	19·5	
				12·0
		0·009	31·5	
				10·5
		0·003	42·0	
				8·0
		0·001	50·0	

* Equal volumes of the two solutions were used in all cases.

It is assumed that the activity of the magnesium ions in solutions diluted with water will be the same as that in solutions diluted with an equal volume of potassium chloride solution. This assumption is not strictly valid since the ionic strength of the solutions is altered by the presence of potassium chloride. However, the effect is negligible for the purpose of these experiments, taking into account the low concentration of potassium chloride used.

The results obtained are shown in Tables VI and VIa and Fig. 4.

It will be seen that the magnesium ion activity, for each of the six sets of determinations was kept constant on one side of the membrane and varied on the other side. The potassium chloride was on the side of fixed magnesium ion activity in three of the experiments, and on the side of variable magnesium ion activity in the other three.

TABLE VI(a)

Inside membrane tube	*Outside membrane tube*		*e.m.f. of cell (millivolts)*	*Differences in e.m.f. (millivolts)*
Mg^{++} activities of solutions before dilution with an equal volume of water	*Mg^{++} and K^{+} activities of the solutions from which the test solution was prepared**			
$a_{Mg^{++}}$	$a_{Mg^{++}}$	$a_{K^{+}}$		
0·243	0·081	0·0081	7·0	
				7·0
	0·027		14·0	
				6·0
	0·009		20·0	
				7·0
	0·003		27·0	
				5·0
	0·001		32·0	
0·243	0·081	0·0027	6·5	
				10·0
	0·027		16·5	
				9·0
	0·009		25·5	
				6·5
	0·003		32·0	
				6·0
	0·001		38·0	
0·243	0·081	0·0009	7·0	
				12·0
	0·027		19·0	
				10·0
	0·009		29·0	
				8·0
	0·003		37·0	
				5.0
	0·001		42·0	

* Equal volumes of the two solutions were used in all cases.

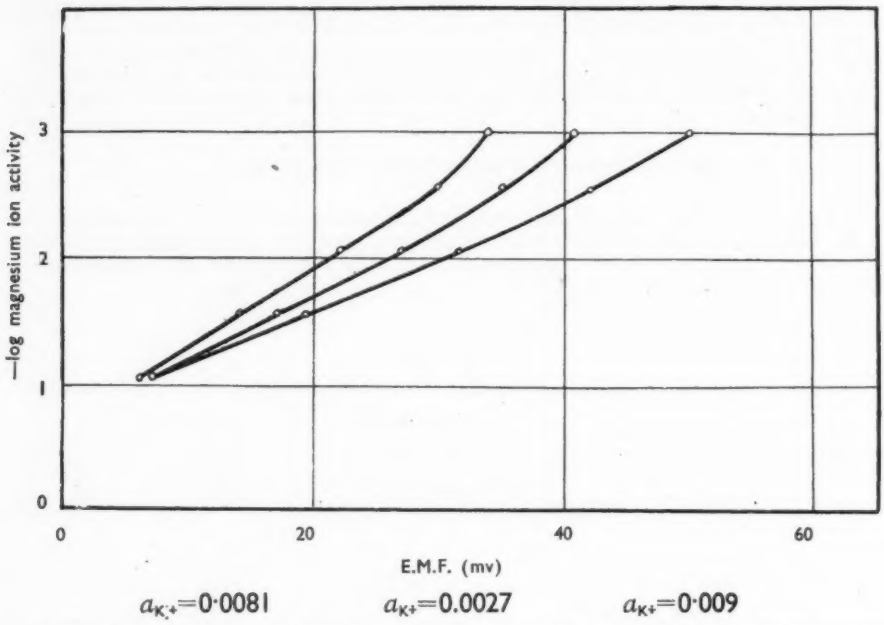

Fig. 4. The effect on the e.m.f. of fluorite membranes produced by the addition of potassium chloride to magnesium chloride solutions.

From the foregoing it is observed that an increase in the concentration of KCl in a magnesium chloride solution results in a decrease in the membrane potential irrespective of whether the KCl is added to the more concentrated or to the less concentrated of the magnesium chloride solutions.

DISCUSSION

At the outset it seems clear that the fluorite membrane electrode will have little analytical use since it appears to be applicable only to solutions containing no other cations than calcium and magnesium. However, it is pertinent to an understanding of the mechanism of membrane electrodes.

The facts which emerge from the foregoing experiments are, briefly, the following:—

1. Reproducible e.m.f. values of the magnitude predicted by the Nernst equation, are obtainable with fluorite membranes in solutions of both calcium and magnesium salts over the activity range 0·1—0·001.

2. Potentials produced by membranes immersed in magnesium salt solutions are reduced by the addition of potassium chloride to one solution.

3. Zero potentials are obtained when fluorite membranes separate solutions of potassium, sodium, ammonium, lead or aluminium salts of different concentrations.

4. Fluorite membranes separating calcium or magnesium salt solutions display a small asymmetry potential.

5. The more concentrated of the two calcium or magnesium salt solutions separated by a fluorite membrane always constitutes the positive side of the cell.

6. The fluorite membranes display a very high electrical resistance, and are impervious to gases, so that they may be considered to be non-porous.

We now wish to consider what light the evidence obtained can throw on the mechanism whereby the membrane electrode potential is established.

The relevant equation of Meyer and Sievers is:—

$$E = \frac{2{\cdot}303\ RT}{2F}\left\{ u \log \frac{x_2 + A.u}{x_1 + A.u} + \tfrac{1}{2} \log \frac{(x_1 + A)(x_2 - A)}{x_1 - A)(x_2 + A)} \right\}$$

where $x = \sqrt{4C^2 + A^2}$

$$u = \frac{U_k - U_a}{U_k + U_a}$$

C = concentration of electrolyte in the external solution
A = concentration of the mobile ions associated with the membrane material, e.g., sodium ions in the case of a sodium clay membrane.
U_k = cation mobility, and
U_a = anion mobility.

In Fig. 5 graphs of E against log C_1/A are shown for different values of $\frac{U_k - U_a}{U_k + U_a}$ ranging from 0·75 to − 0·5, taking $A = 1$ and $C_2 = 3C_1$.

The experimental curves obtained with fluorite membranes in solutions of calcium and magnesium salts (see Fig. 3) correspond in shape with these theoretical curves, but not in sign. Since the sign of the theoretical curves is based on the postulation of an immobile anion, the experimental results indicate that the immobile ion is the cation.

Anderson[5] also found the sign of fluorite membrane electrodes to be such as to require the immobilization of the cation rather than the anion. He suggested that the membranes function as "crack" electrodes by the establishment of junction potentials in small cracks in the membranes. Since, in aqueous solution, the anions are more mobile than the cations involved in these investigations, this, at first sight, would seem to be possible.

Anderson's theory must be discounted for the following reasons:—

(i) The potentials obtained with fluorite membrane electrodes in solutions of known magnesium or calcium ion activities are so high as to require the complete immobility of one ion. In the Nernst equation for diffusion potentials,

$$E = \frac{RT}{2F} \cdot \frac{U_k - U_a}{U_k + U_a} \ln \frac{C_2}{C_1}$$

the values of E of 13·8 mv. which were obtained for $\frac{C_1}{C_2} = \frac{1}{3}$ require that $\frac{U_k - U_a}{U_k + U_a} = 1$.

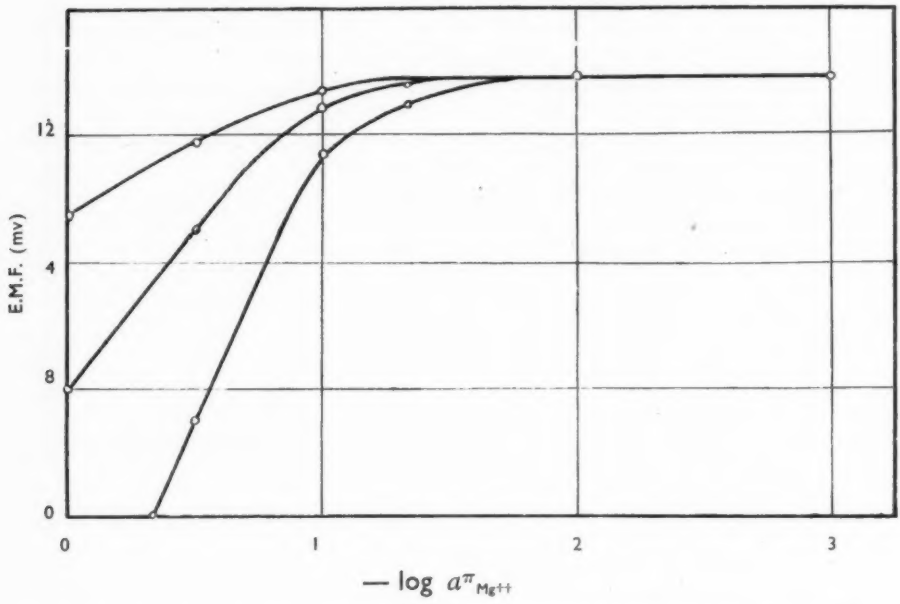

Fig. 5. Variation of e.m.f. with magnesium ion activity, calculated from Meyer and Sievers equation.

Thus either U_k or U_a is zero. From the sign of the e.m.f. it follows that $U_k = 0$.

(ii) The existence of liquid junctions does not seem likely in view of the high electrical resistance and impermeable nature of the membranes.

The fundamental question now arises as to the manner in which the immobilization of the cation occurs.

The Meyer and Sievers theory involves the transport of current through the membrane by only one ion. Therefore it would seem desirable to see whether this is consistent with our knowledge of the mechanism of conduction through crystals. Measurements have been made of the transport numbers of the ions in ionic crystals[7], and it has been found that in the majority of cases, except where the temperatures are very high, the current is carried entirely by one of the ions. No measurements appear to have been made on calcium fluoride, but with both barium chloride and barium fluoride it is the cation which is mobile. However, nearly all these measurements of transport numbers have been carried out at temperatures above 200° C.

At room temperature conduction in ordinary crystals is due to a "structure sensitive" or "secondary" conduction process, as opposed to the "structure insensitive" process found in pure crystals, especially at higher temperatures. As Mott and Gurney[8] point out,

"if the mechanisms are quite different, the ions which take part in the secondary conductivity may have the same sign as those which are mobile at high temperatures, or they may be ions of opposite sign". In either case it seems probable that only one ion will move in the conduction process.

Therefore, it would seem that the potential differences met with in the experiments on fluorite membranes in calcium or magnesium salt solutions could well be accounted for by the theory of Meyer and Sievers, which does not appear to be inconsistent with our information on the mechanism of conduction by ionic crystals.

The reduction of the above-mentioned potential differences by the presence of potassium chloride in the solution is also perhaps explicable along similar lines. It is known that the conduction of ionic crystals is extremely sensitive to impurity in the crystal, and it has even been suggested that the low temperature conduction process is due entirely to impurities[9], the amounts required to give the observed effects varying from one part in 10^5 to one part in 10^8. Therefore, it is possible that the potassium ion is capable of entering into the fluorite crystal and conducting part of the current, thus lowering the transport number of the fluoride ion below the value of 1·00. This process does not demand that potassium ions be able to replace calcium ions in the lattice, because con duction is actually due to the movement of lattice defects.[10]

An explanation of the membrane processes could perhaps be based on adsorption, where, if the fluorite adsorbs positive ions it would acquire a positive charge (comparable with the selectivity constant A postulated by Meyer and Sievers) which would then tend to repel other positive ions. The Paneth-Fajans-Hahn rule would lead us to expect that magnesium and calcium ions would be adsorbed. Willis[11] and Hartung[12] have shown that for porous membranes selectivity is proportional to adsorbtion. The falling off of e.m.f. at higher concentrations of calcium or magnesium or in the presence of potassium chloride could perhaps be accounted for by lowering of the electrokinetic potential by the increased concentration of anions, thus lowering the effective charge. However, this leads to several difficulties:

(i) The low ionic strength at which potassium chloride is effective in lowering the measured e.m.f.

(ii) The fact that replacement of monovalent anions by the divalent sulphate ion has no effect on the measured e.m.f.

The above considerations dealt with the possible mechanisms whereby flourite membrane electrode potentials are established in solutions of calcium and magnesium salt solutions, and the lowering of these potentials by the presence of potassium chloride. It will be remembered, however, that when the membranes were placed between solutions of sodium, ammonium, potassium, lead or aluminium halides of different concentrations the potentials observed were actually zero. On the basis of the Meyer and Sievers theory involving the transport of ions through membranes, it would thus appear that the flourite membranes are permeable to lead, aluminium and potassium ions, but not to calcium or magnesium ions, which is not a very plausible explanation since there is no obvious reason why magnesium ions, for instance, should be immobilized while lead ions are not.

This is a most surprising result and is difficult to account for. There are in fact only two possible explanations, namely that either:—

(i) the transport numbers of the positive and negative ions carrying the current across the boundary between the two solutions are exactly equal in all cases except those of calcium and magnesium salts or,

(ii) there are two potentials set up somewhere in the system that exactly compensate each other. The first explanation seems highly improbable. Compensating electromotive forces, on the other hand, might well be developed at the opposite crystal faces, but it is difficult to suggest any mechanism which would lead to such an effect.

It is evident that the information at present available is not sufficient to form the basis of an explanation of the phenomena observed. In addition to further experiments of the type reported in this paper, more research is required into the nature of the conduction process occurring in calcium fluoride crystals at room temperature. A study of the surface and electrokinetic properties of fluorite might also be of value.

The authors wish to acknowledge their indebtedness: to Professor H. Stephen, O.B.E., for his interest in the work; to Dr. K. A. Murray for his helpful guidance and criticism, especially during the period that one of us (R.A.) was absent overseas; and to the Council for Scientific and Industrial Research, for a grant-in-aid to one of us (M.M.).

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AN AUTOMATIC RECYCLING CONDUCTANCE WATER STILL.

by

A. FAURE, P. K. FAURE AND J. A. GLEDHILL

OPSOMMING

'n Elektries verhitte distilleerapparaat waarin die water in twee stadia gedistilleer word, eers uit alkaliese permanganaat en dan uit fosforsuur, word beskryf. Toebehore wat 'n konstante waterpeil en veiligheid verseker word gebruik sodat die apparaat lang tydperke sonder aandag kan werk. 'n Outomatiese toestel laat die water sirkuleer as dit nie uit die opvangsfles verwyder word nie; gevolglik word die lang opwarmingsperiode wat noodsaaklik is in die geval van die gewone distilleerapparate, vermy. Daar word ook aangetoon dat die verwydering van ammoniak uit die distilleerketel gevolg deur die verwydering van koolstofdioksied uit die geleiding-sel beter resultate lewer as wanneer albei gasse-tegelyk uit die distilleerketel verwyder word. Hierdie distilleerapparaat lewer water met 'n geleidings vermoë van minder as 0·09 mikromhos per centimeter; die beste monsters het 'n waarde van 0·071 bereik. Die apparaat verskaf ongeveer 16 liter water per dag.

SUMMARY

An electrically heated still is described in which the water is distilled in two stages, first from alkaline permanganate and then from phosphoric acid. Constant-level and safety devices are employed to enable the still to run for long periods without attention. An automatic device allows the water to be recycled when none is being taken from the still, thus avoiding the long "warm-up" period necessary with conventional stills. It is pointed out that removal of ammonia in the still and of carbon dioxide in the conductance cell gives better results than removal of both gases in the still. When used in this way the water from the still has a conductivity below 0·09 micromhos per centimetre, the best water obtained reaching 0·071. The still will deliver up to 16 litres of such water per day.

The work reported in this paper is part of a research programme originated by Professor W. F. Barker in this laboratory.

In the execution of this programme, recent measurements of the conductances of very dilute aqueous solutions of electrolytes have necessitated the use of water of the lowest conductance attainable in routine work. The literature abounds with descriptions of stills for the production of conductance water; in their original forms several of these are capable of delivering daily several litres of "ultra-pure" water of conductivity better than 100 nm. per cm. (1 nm per cm. = 1 nanomho per centimetre = 10^{-9} $ohm^{-1}cm^{-1}$) at 25° C. In general use, however, these stills do not seem to perform quite as well as this, and the common range of conductivity of the water used in precision conductance research has been from 200 to 600 nm. per cm.

It is commonly found that the water obtained from a still improves in quality from the time of starting the distillation, and reaches its lowest conductivity after several hours; this effect is probably due to the leaching out of those parts of the still which have not been in contact with water for some time. The still described in this paper is arranged to operate automatically for several weeks, the water, once it has filled the collecting vessel, being siphoned back into the reservoir. In this way it is possible to obtain water of excellent quality as it is required, without having to wait for the still to be leached out.

The hydrogen and hydroxyl ions present in water contribute 55 nm. per cm. to its conductivity at 25° C.; it is generally believed that the remainder is due to carbon dioxide in the water. Work carried out in this laboratory has suggested that a large part of the residual conductivity is due to the ammonium and bicarbonate ions formed from the small amounts of ammonia and carbon dioxide in the air. This work, to be published later, also suggests that, while residual carbon dioxide is easily removed from the water by a current of carbon-dioxide-free gas, this procedure does not effectively remove it if ammonia is present. Hence it is desirable to remove all the ammonia before the water is used, a fact which has been stressed by Bjerrum[1] and by Ellis and Kiehl[2] among others.

In the present still a second distillation of the water from phosphoric acid solution is used to accomplish this end. The use of this acid in the preparation of conductance water has been suggested from time to time (e.g., by Bourdillon[3]), but the decision to use it in the present case was taken on the basis of the excellent results obtained by Ellis and Kiehl[2] in their work on the pH of distilled water, and has been fully justified by the performance of the still.

By the technique in which the ammonia is removed in the still and the carbon dioxide is removed later in the cell we have found it possible to use water of conductance 80—90 nm. per cm. as a routine practice. Many stills previously described in the literature as capable of delivering water of conductivity less than 70 nm. per cm. use a counter-current of purified air or condense only a fraction of the steam in order to free the water from gaseous impurities. The water is then used in the conductance cell without further blowing out. Careful study of later papers from those laboratories in which such stills were used, however, has failed to disclose any reports of experimental work in which the conductivity of the water was less than 120 nm. per cm.[4]

Description of the still

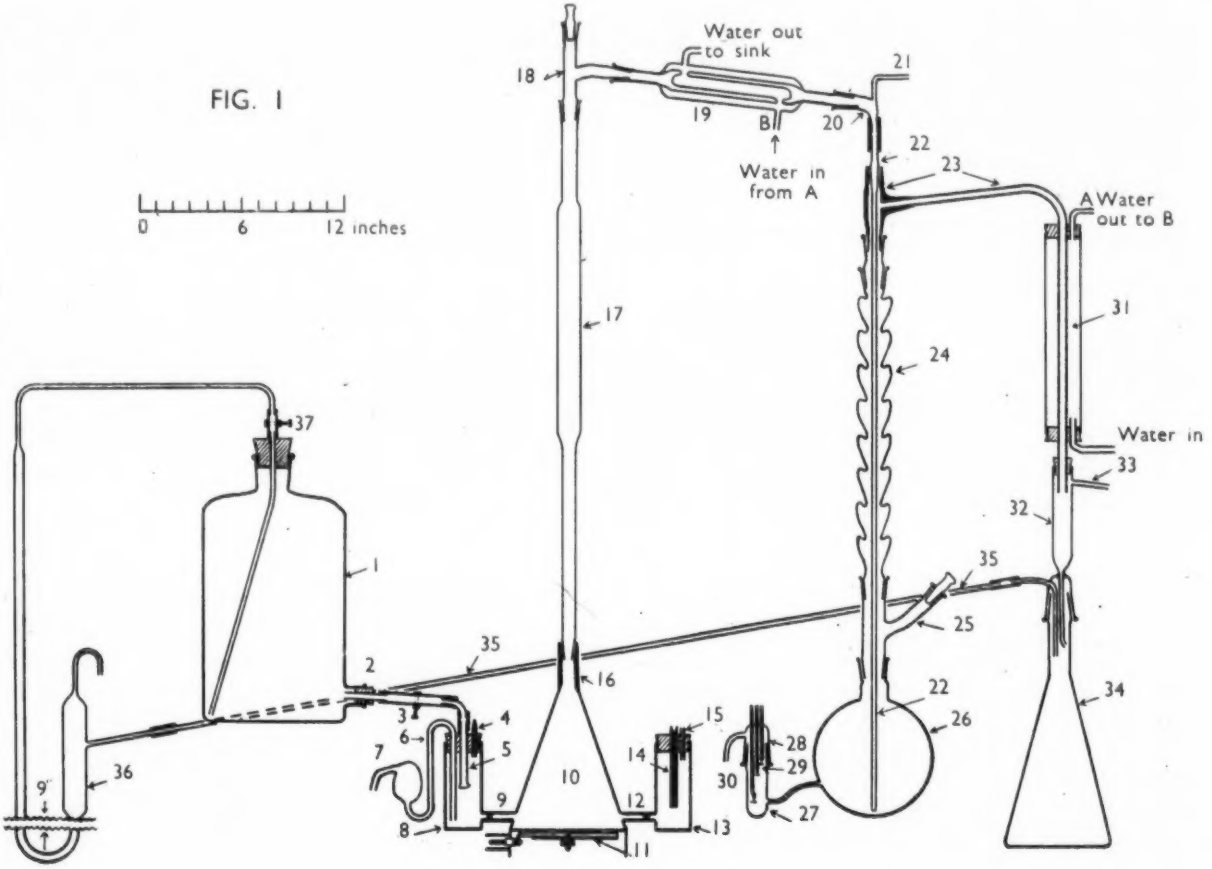
Figure 1 is a diagram of the still. The water for distillation is contained in the 10 litre Pyrex aspirator 1, from which it flows through the constant-level device to the boiler 10. The latter is an 18—8 stainless steel conical vessel with two side cups 8 and 13 of the same material, which are welded to the connecting tubes 9 and 12. These connecting tubes are made of ½-inch stainless steel rod and have for ½ inch of their length holes of diameter 1/32 inch, connecting the ⅜ inch holes from either end; the purpose of the small holes is to permit slow transfer of liquid through the tubes without allowing the level in the cups to change rapidly as the liquid in 10 swishes round when boiling.

The cup 8 carries, through a rubber stopper, the inlet tube 5, the height of which determines the level of liquid in 8, 10 and 13. It also carries the level-indicator tube 6 and the air-leak tube 4 which consists of a short length of capillary tubing drawn to a diameter of about 0·3 mm. The tube 5 is flared at its lower end and has a spout like that of a beaker at one side. When the level in 8 falls below the end of this tube, bubbles of air enter and travel up into 1 by way of the slightly inclined tube 2, allowing water to enter 8 and so hold the liquid level constant. By having the small air leak 4 and the wide portion 7 on the level-indicator, liquid flows back from 7 into 8 during the bubbling process and so limits the amount of water entering to a quantity which can be handled by the cup and connecting tube 9. The overflow on 7 is a safety device in case air should get into 1 by some mishap; it discharges into a sink.

The boiler 10 contains enough sodium hydroxide to make the solution about normal, and enough potassium permanganate to make it about decinormal; the purpose of this mixture is to oxidize organic matter in the water and to hold back acid impurities. Because of the rapid action of the mixture on glass, it is essential to have the boiler made of some resistant material: the 18—8 stainless steel has been found eminently satisfactory for this purpose. The boiler is heated by a 900 watt urn element 11, which is controlled through a safety relay in conjunction with the electrode 14 as described later.

At the top of the boiler is the standard-taper socket 16, turned from stainless steel and welded to the boiler; it is designed to take the B24 joint at the foot of the spray trap and reflux column 17. This is surmounted by the stillhead 18, condenser 19 and adapter 20, all of which have standard-taper joints. The adapter connects with the inlet tube 22

FIG. 1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to the second boiler 26 by a glass-to-glass joint in pressure tubing, which gives a little flexibility when assembling the still. The lower end of 22 is drawn down to about 1mm. diameter to prevent solution from 26 blowing up and back into 10 if severe bumping should develop. The adapter carries also a tube 21 which is connected to a 2 litre flask (not shown) which communicates with the air. This flask acts as a buffer to prevent excessive "breathing" of laboratory air during boiling. Provision is made for a guard tube on the inlet.

The second boiler 26 is a 2 litre round-bottomed flask with the control device 27 sealed on by way of a length of 0·7 mm. capillary tubing, and is heated by a two-element flask-heating oven of special design. This flask contains approximately 0·1 M. phosphoric acid solution. It is connected by means of a B34 joint to the adapter 25, which carries the pear-bulb fractioning column 24 to act as a spray trap and reflux device, and which also has a side arm through which a porcelain chip may be inserted if bumping commences. Above the fractionating column is the cast block-tin stillhead 23, which has standard half-taper joints to fit the column and to carry the inlet tube 22. The tin take-off pipe from the stillhead is inclined upwards so that the first condensate will return to 26. The steam is finally condensed in the vertical portion 31, from which it falls through the adapter 32 into the 2 litre conical collecting flask 34, which has a B34 cone joint to fit the cap on the adapter as shown. The tube 33 connects with a 1 litre buffer flask which communicates with the air through a guard tube containing soda lime (for CO_2 and HCl), cupric chloride dihydrate (for H_2S), solid metaphosphoric acid (for NH_3) and more soda lime, in that order from the i nside.

When the flask 34 has filled, the water is forced through the recycling tube 35 by the head which builds up in 32, and siphons intermittently down the sloping tube into the bulb 36. Since the latter is connected with the reservoir 1 by way of 37, the natural level of the water in 36 is the same as that in 8; thus when returned water runs into 36 it is eventually transferred to 1 to take the place of water leaving through 2, and becomes recycled. Provision is made for a guard tube at the top of 36.

The apparatus is mounted on a framework of three cross-braced retort stands screwed to a wooden base; a wooden stand is provided for the aspirator 1.

The electrical control apparatus

Since the still is required to operate unattended for long periods it is necessary that it should be protected against various kinds of fault which may develop. Also, it will be evident that some means is necessary for ensuring that water distils off from the second boiler 26 at a rate equal to that at which it enters from 10, otherwise 26 will fill and overflow or boil dry and crack. Both these ends are achieved by the use of a simple electrical control system.

The boiler 26 is heated by a specially made hotplate containing two elements, one o 750 watts and one of 600, spirally wound on an alundum base shaped to fit the flask. The 750 watt element is permanently on, but both it and the 900 watt element 11 of the first boiler form the load of a Sunvic type F 102–4 hot-wire relay. The control circuit of this relay is modified so as to connect to the line on one side and to the electrode 30 in the control device 27 on the other side. Electrode 29 is connected to the stainless steel electrode 14 in the control device 13 of the first boiler, and the metal boiler itself is earthed (Figure 2). This ensures that the permanent heaters will only function if the liquid level in 13 is above the end of the electrode 14 and if the level in 26 is sufficiently high to cover electrode 29. If the supply of water from 1 should fail for any reason, or

if 26 should crack, this control circuit will at once switch off the heaters. Also, because of the connexion *via* earth and the neutral wire, the still cannot be put into operation if the earth contact on 10 is faulty, nor if the mains plug is inserted the wrong way round.

An automatic recycling conductance water still

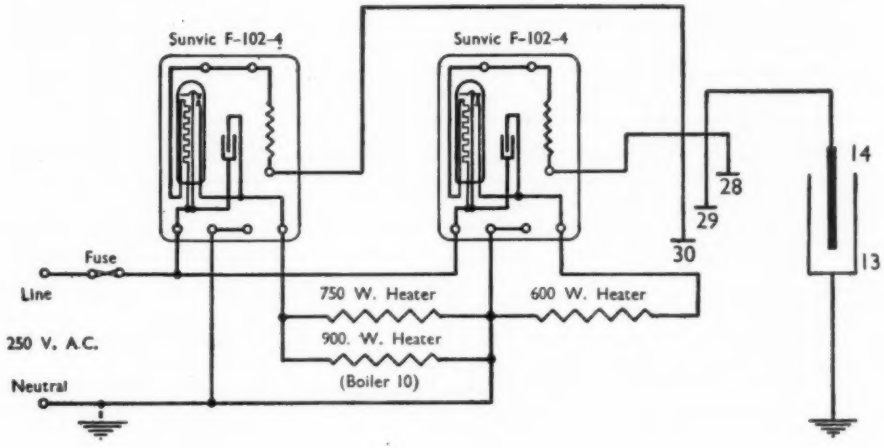

FIG. 2. Electric control circuit

The 600 watt intermittent heater for flask 26 is controlled through a similar Sunvic relay, the control circuit of which operates through electrodes 28, 29 and 14 to earth. Thus when the fast distillation from 10 brings the liquid level in 26 to that of electrode 28, the second heater is energized and, since the total wattage input to 26 now exceeds that to 10, the level falls again until contact with 28 is broken, and flask 26 refills until the cycle starts again.

The electrodes 28, 29 and 30 are horizontal pieces of thick platinum foil of area about $\frac{1}{4}$ square centimetre, with stout leads which are sealed to the mercury-filled Pyrex lead-tubes by Corning 707 glass and uranium glass.[5] The lead-tubes are brought out by internal seals through a cap with a B34 socket, making the electrode assembly easily removable when the still is to be cleaned. Electrode 14 was originally constructed in a similar way, but was found to be attacked by the caustic soda so that the platinum wire became loose and the electrode fell out of the glass tube. It was replaced, therefore, by a stainless steel rod as shown. It is not practicable to have this electrode in cup 8 and thus to eliminate one of the two cups, because when the still recycles, 8 is full of very pure water which does not conduct well enough to close the circuit.

Performance

The still delivers 2 litres of water into the receiving flask in 3 hours, so that 16 litres a day may be obtained from it if desired. Normally it is allowed to recycle overnight, and the convenience of having a flask full of good conductance water first thing in the morning would alone justify the continuous operation principle. Ordinary laboratory distilled water is used to fill the reservoir 1 when necessary. The pinchcocks 3 and 37 are first closed and afterwards opened slowly to prevent overflow of solution from 7. When poured from the flask into the cell in the air of the laboratory the water has a conductivity of about 800 nm. per cm.; after blowing out with carbon-dioxide-free air for about an hour, the time depending on the bubbling rate, the conductivity falls to a minimum which is between 80 and 90 nm. per cm. The best sample measured had a conductivity of 71 nm. per cm. This may be compared with the value of 62 nm. per cm. (recalculated to 25° C.) reached by Kohlrausch and Heydweiller in their classical experiment which involved 42 distillations *in vacuo*,[6] and with the figure of 66 nm. per cm. for the best water obtained by Kraus and Dexter from their still.[7]

When the water is kept in well-seasoned Pyrex flasks with tinfoil-covered rubber stoppers its conductivity increases by less than 1 nm. per cm. per day at 24° C. In a cell where it is agitated by bubbling the rate of increase is somewhat higher.

The chemicals in the boilers need replacing every month, or whenever the quality of the water starts to fall off.

Work on the early forms of the still was done in conjunction with Mr. G. N. Festenstein, MSc.

We are indebted to Mr. G. McP. Malan, BSc. for criticism and suggestions, and for a large number of measurements of the conductivities of samples of water.

One of us (A.F.) held a research studentship awarded by African Explosives and Chemical Industries during the period of development of the still, and wishes to express his gratitude to that company.

Note added in proof: Since submitting this paper the figure of 71 nm. per cm. for the best water has been improved upon by using purified nitrogen instead of air for the stirring gas. The best water obtained in this way reached 62 nm. per cm.

To guard against failure of the town water supply to the condensers a perforated bucket on a pivoted arm carrying a mercury switch has been inserted between electrodes 29 and 14, and the outflow water from the condensers passes through this bucket. This device has proved its worth on several occasions.

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THE NITRIC ACID OXIDATION OF COAL
PART II. THE ETHER-INSOLUBLE CONSTITUENTS:- THE HUMIC ACIDS AND THE NEUTRAL ETHER-INSOLUBLE PRODUCT

by

B. L. VAN DUUREN

OPSOMMING

Daar is bevind dat die eter-onoplosbare deel van die oksidasieproduk van steenkool met salpetersuur (vgl. Deel I) tot die humiensure of nitrohumiensure wat in die literatuur beskrywe is, behoor. Eksperimente op hierdie produk, die chromatografiese skeiding van die mengsel en die afskeiding van 'n neutrale eter-onoplosbare produk word beskryf.

SUMMARY

The ether-insoluble material obtained from the nitric acid oxidation of coal (Part I) was found to be similar to the humic acids and nitrohumic acids described in the literature. Some chemical investigations on the mixture and the chromatographic separation of its constituents is discussed. A neutral ether-insoluble product was separated from the oxidation product.

In the previous communication (Part I) the separation of the methyl ethyl ketone-soluble oxidation product into an ether-soluble and an ether-insoluble fraction by extraction with ether was described. The ether-insoluble product constituted 35 per cent. of the methyl ethyl ketone-soluble product.

This brown, amorphous product consists entirely of acidic substances since no material could be extracted from alkaline solutions with organic solvents. It is insoluble in hydrocarbon and halogenated hydrocarbon solvents, slightly soluble in water and more soluble in ketones (acetone and methyl ethyl ketone) and alcohols (methanol, ethanol and butanol — 2). The product contains nitrogen, but no sulphur. It does not melt, but decomposes above 350° C. It yields no distillable products at elevated temperatures either at atmospheric pressure or under a high vacuum. Decomposition products consist of gaseous products (carbon dioxide and water) and a black carbonaceous residue.

Products of this nature have been termed humic acids. Those obtained from the nitric acid oxidation of coal have been termed nitro-humic acids[1–16]

Preliminary experiments on the chromatography of this product indicated that it consisted of a mixture of substances. Prior to chromatographic separation, however, a number of experiments were carried out on the mixture as such in order to obtain more general information regarding the nature of the product.

It must be pointed out at this stage that the results obtained from these experiments are of a qualitative nature only, which is to be expected in view of the heterogeneous nature of the ether-insoluble product.

(*a*) The action of concentrated nitric acid

According to Howard[17] and Francis[18] the oxidation of coal takes place in stages, the humic acids constituting intermediate products in the oxidation process. These acids were supposed to decompose further through acids of unknown constitution and lesser complexity to form simple aliphatic—and aromatic carboxylic acids.

It has been pointed out, however, by various workers [19, 20, 21] that the oxidation of coal with one particular reagent gives finally a humic acid mixture of "limiting composition".

Prolonged treatment of the ether-insoluble acids obtained in the present investigation, with concentrated nitric acid yielded brown amorphous ether-insoluble products of almost constant composition. (See Table I).

At first sight, therefore, it seems that the ether-insoluble acids are derived from one particular part of the coal structure and that the complex acids of unknown constitution which are undoubtedly present in the oxidation product, and the simple carboxylic acids, the isolation of which was described in Part I, do not necessarily represent degradation products of these humic acids.

It must be born in mind, however, that the humic acids can be degraded further by other oxidizing agents to yield simpler products [3, 5, 20, 21] of the same type as have been obtained in the present investigation.

From this latter fact emerges the speculation that the coal structure is more uniform than one is led to infer from the former evidence. The humic acids, formed as primary oxidation products may be degraded to some extent to simpler products (mentioned above) but, further degradation is apparently prevented by stabilization of the humic acid structures by the reagent itself.

Such a view would be more in accord with the evidence regarding the chemical constitution of coal as obtained by other methods of investigation.

(*b*) The action of alkali

The mixture of humic acids as obtained from the oxidation product was found to be only partially soluble in acetone and alcohol. However, if the product was dissolved in alkali and the alkaline solution acidified immediately, a product was obtained which was completely soluble in both solvents but still ether-insoluble.

The alkali appeared to effect some chemical change, the most probable being the hydrolysis of anhydrides and/or lactones. The observed increase in the oxygen content, and the observation that mild heating (100° C.) of the ether-insoluble product decreases its solubility in acetone and alcohol, support such a view. The percentage compositions appear in Table 1.

TABLE I

Analysis of nitric acid-treated ether-insoluble products after action of alkali

Product	C	H	N
Original product (1)	50·8	2·5	3·8
(i) after treatment with alkali	45·8	3·2	3·6
(ii) „ „ „ HNO_3 for 27 houas ...	51·4	2·4	4·8*
(iii) „ „ „ „ „ 52 „ ...	50·9	2·6	5·3*

* The increased nitrogen content may be due to further introduction of nitrogen-containing groups.

The presence of carboxyl-groups or carboxyl and hydroxyl groups in ortho-position to one another would be more than likely in a condensed cyclic structure containing a considerable number of carboxyl-groups and some hydroxyl-groups (see (*c*) below).

(*c*) Methylation

The presence of both hydroxyl and carboxyl-groups in humic acids has been proved by various methods. Fuchs and Sandhoff[13] have examined these methods critically. The methylation of various nitrohumic acid preparations has led to the following results:

TABLE II

Methoxyl content of methylation products

Total per cent. OCH_3	*Per cent Ether OCH_3*	*Per cent Ester OCH_3*	*Reference*
15·2	6·2	9·0	[4]
19·0	9·4	9·6	[4]
10·8	5·2	5·6	[13]

According to Fuchs and Sandhoff (*loc. cit.*) all the hydroxyl groups are acidic in nature.

In the present investigation various methods of methylation were employed. The results are tabulated in Table III.

TABLE III

Methoxyl content of methylation products of various methods of methylation

Method of methylation	*Total per cent OCH_3*	*Per cent ether OCH_3*	*Per cent ester OCH_3*
1. Methanol and hydrochloric acid followed by diazomethane ...	17·2	—	—
2. Diazomethane alone	16·95	6.3	10·6
3. Dimethylsulphate followed by diazomethane	17·7	—	—

It is doubtful whether aliphatic hydroxyl groups will be present as such in view of the drastic nitric acid treatment to which these products have been subjected. Nevertheless, the presence of alcoholic hydroxyls through tautomerization of $0 = \overset{\backslash}{C} - \overset{\backslash}{C}H_2$ to $- C(OH) = \overset{\backslash}{C}H$ has been suggested by Fuchs [4, 5].

(*d*) Reduction with zinc dust and hydrochloric acid

The dark-coloured amorphous product obtained was separated chromatographically into two fractions. The percentage compositions and atomic ratios of these products are given in Table IV.

TABLE IV

Analysis of reduced products

	C	*H*	*N*	*O*
Fraction I Percentage composition	60·8	4·9	2·8	31·5
Atomic ratio	1·0	0·96	0·039	0·39
Fraction II Percentage composition	54·7	5·7	1·4	38·2
Atomic ratio	1·0	1·26	0·021	0·52

Apart from the lower oxygen and higher hydrogen content of the reduction products, as compared with the original material (See Table I), a marked decrease in nitrogen is noticed.

Empirical calculations indicate further that if the nitrogen of the reduced product is assumed to be present as amino-groups, then other reduction reactions besides the reduction of nitro to amino groups, must have taken place.

(*e*) Oxidation of the product from (*d*) above with nitric acid

The light yellowish-orange amorphous product obtained from this reaction gave the following percentage composition on analysis:—

C, 51·2; H, 3·1; N, 4·1%,

from which the atomic ratios were calculated to be:—

C, 1·0; H, 0·72; N, 0·068; O, 0·61.

Comparing these values with those given in Tables I and IV it is observed that the nitrogen content is higher than that of the reduced products and about the same as that of the original mixture of ether-insoluble acids.

There is also a possibility that a part of the nitrogen present in this product is in the form of oxonium compounds formed between heterocyclic oxygen atoms and nitric acid molecules.

(*f*) Decarboxylation in quinoline

During this experiment carbon dioxide was evolved and a chocolate brown, amorphous product, which gave the following percentage composition and atomic ratios was formed:—

C, 65·95; H, 3·4; N, 7·5%.
C, 1·0; H, 0·63; N, 0·098; O, 0·26.

In view of these results it appears that the decarboxylation is accompanied by condensation reactions involving also the loss of water molecules. This will be more than likely in view of the following considerations:—

(i) Favourable conditions for condensations exist in the decarboxylation process, which is carried out in quinoline at an elevated temperature.

(ii) The decarboxylation product is totally insoluble in all ordinary organic solvents (alcohols, ethers, ketones, hydrocarbons, etc.), water and alkali, but was found to be soluble in pyridine.

(iii) The low methoxyl content of the diazomethane methylation product, 6·58 per cent., indicates a decrease in hydroxyl groups which would be involved in condensation reactions.

Chromatographic separation

Although the chromatographic method has been applied for the investigation of coal extracts by Lahiri[22] no attempt has apparently been made as yet to apply the technique to separate the humic acids obtained from coal oxidation experiments. One would expect, in view of the close similarity in properties exhibited by the components of these mixtures, that they consist of compounds which are closely similar chemically; differences in structure existing most likely only in the number and positions of peripheral groups.

In preliminary tests, the mixture was found to be adsorbed too strongly on alumina for separation but could be separated into five distinct fractions using cellulose as adsorbent. These fractions, although resembling one another in certain properties, viz.

amorphous nature, thermal behaviour and insolubility in ether, differed in colour and solubility in acetone, alcohol and water.

From combustion data the percentage compositions, empirical formulae and atomic ratios given in Table V were calculated. The empirical formulae were calculated on a C_{60}—basis for purposes of comparison only. The close resemblance between the percentage compositions calculated from analyses and those calculated for the empirical formulae (see experimental section) is remarkable.

TABLE V

Analysis of chromatographic fractions

Fraction number		*C*	*H*	*N*	*O*	*Empirical formula*
I	(*a*)	50·9	3·1	4·1	42·0	
	(*b*)	1·0	0·70	0·068	0·61	$C_{60}H_{40}N_4O_{35}$
II	(*a*)	50·0	2·8	3·8	42·4	
	(*b*)	1·0	0·67	0·065	0·65	$C_{60}H_{40}N_4O_{35}$
III	(*a*)	54·0	3·25	2·9	39·9	
	(*b*)	1·0	0·72	0·044	0·55	$C_{60}H_{40}N_2O_{34}$
IV	(*a*)	56·5	2·7	3·2	37·6	
	(*b*)	1·0	0·58	0·049	0·50	$C_{60}H_{34}N_2O_{31}$
V	(*a*)	35·8	4·2	3·5	56·45	
	(*b*)	1·0	1·41	0·083	1·18	$C_{60}H_{80}N_5O_{70}$

(*a*): percentage compositions.
(*b*): atomic ratios.

The following features of this table are noteworthy:—

(*a*) There appears to be a close similarity between fractions I and II, and III and IV respectively.

(*b*) The carbon: hydrogen ratios throughout point to a condensed cyclic structure.

(*c*) The atomic ratios for fraction V are quite different from those for the other fractions.

(*d*) The relation of the analysis given above to those given by other investigators are interesting. Typical values for the ultimate analysis of nitro-humic acids are given in Table VI.

TABLE VI

Ultimate analyses of nitrohumic acids

Per cent C	*Per cent H*	*Per cent N*	*Reference*
53·8	3·6	2·2	[9]
59·9	4·3	2·9	[9]
60·9	4·2	3·8	[11]
57·2	3·7	3·1	[12]
58·9	4·4	5·7	[13]

Comparing these values with those given in Table V, the lower carbon- and higher oxygen content of the humic acids under investigation is remarkable.

The five fractions discussed above were methylated with diazomethane. The percentage methoxyl lies between 13·5 and 18·2 per cent. for the different fractions.

The neutral ether-insoluble product

During the investigation of the neutral fraction of the ether-soluble fraction of the oxidation product (to be discussed in a subsequent communication) a small amount of a neutral, amorphous, ether-insoluble product was isolated. This product constitutes 0·4 per cent. of the ether-soluble fraction i.e. 0·26 per cent. of the methyl-ethyl-ketone-soluble oxidation product. This product had presumably been dissolved by the oils present in the ether-soluble fraction since no trace of it could be found in the ether-insoluble fraction. The separation of this product is of significance since no compounds of this type have as yet been met with in a survey of the literature on the nitric acid oxidation of coal. From combustion data the following empirical formula was calculated for this product:—

$$C_{60}H_{46}N_9O_{32}.$$

The diazomethane methylation product contained 9·50 per cent OCH_3. No further investigations have as yet been conducted on this product.

CONCLUSION

The ether-insoluble product consists of a chromatographically separable mixture of chemically similar compounds which are acidic in character. The acidity is due to both carboxyl and hydroxyl groups, some of which are probably in ortho-position to one another giving rise to anhydridization and lactonization. The carbon hydrogen ratios indicate a condensed type of structure.

About one half of the total oxygen can be accounted for in hydroxyl and carboxyl groups, the rest existing most likely in the following:—

(*a*) Heterocyclic and linear oxygen bridges.

(*b*) Nitro and isonitroso groups.

(*c*) Carboxyl groups.

The nitrogen exists for the greater part in nitro-, isonitroso-, or oxonium structures and probably to a small extent as heterocyclic nitrogen.

The failure of nitric acid to degrade the humic acids further may be due to stabilization of the same by the nitric acid itself, thus preventing further degradation.

(*a*) The action of concentrated nitric acid

The ether-insoluble material (I) (10g.) was refluxed with concentrated nitric acid (100 ml.) for 27 hours. Removal of the acid under reduced pressure left 9·1g. of a brown amorphous ether-insoluble product (II). 5g. of the latter was similarly treated for a further 25 hours. The resulting product (III) (4·6g.) was also ether-insoluble.

(*b*) The action of alkali

The original product (I) (40g.) was dissolved in dilute caustic soda solution (500 ml.; 2·5N), and dilute hydrochloric acid (100 ml; V/V) was added. A yellowish-brown flocculent precipitate gradually separated. The aqueous suspension was extracted with methyl ethyl ketone (1l.) and the solvent removed under reduced pressure. The dark brown amorphous product (IV) (36g.), completely soluble in acetone and alcohol, was

purified by precipitation from an acetone solution with ether. This procedure was repeated three times and the product finally dried in a high vacuum at 50° C. for 3 hours. Products II and III of (*a*) above were treated in a similar manner.

Analyses

I Found: C, 50·8; H, 2·5; N, 3·8 %.

II Subsequent to alkali treatment:
Found: C, 51·4; H, 2·4; N, 4·8 %.

III Subsequent to alkali treatment:
Found: C, 50·9; H. 2·6; N, 5·3 %.

IV *Found: C, 45·8; H, 3·2; N, 3·8 %.

(* In all subsequent experiments this product was used as starting material).

(*c*) **Methylation**

These were carried out by various methods:—

(i) Methanol in presence of hydrochloric acid gas followed by diazomethane:— The reprecipitated ether-insoluble material (1g.) was suspended in dry methanol (25 ml.) and boiled under reflux for one hour in an atmosphere of dry hydrochloric acid gas. The resulting solution was boiled under reflux for an additional hour, the solvent removed by distillation and the residue dissolved in acetone (25 ml.). A solution of diazomethane in ether at 0° C. (0·25 g. in 50 ml. ether) was added to the cooled acetone solution of the methylated product. A copious evolution of gas ensued and a brown flocculent precipitate settled out. The solution was allowed to stand in ice for 3 hours with occasional shaking and then at room temperature for 12 hours. The product was purified and dried as described above.

(ii) Methylation with diazomethane alone:— The original product was methylated with diazomethane alone, the methylation product purified and dried in exactly the same way as for (i) above.

(iii) Methylation with dimethyl sulphate followed by diazomethane:— The reprecipitated ether-insoluble product (0·5g.) was suspended in acetone (5 ml.), anhydrous potassium carbonate (0·25g.) was added and the mixture boiled under reflux whilst adding small amounts of dimethyl sulphate at a time. When all the dimethyl sulphate had been added (0·30g.) some more potassium carbonate (0·1g.) was added and the mixture boiled under reflux for a further period of 5 hours. The precipitate was filtered, washed with acetone and the filtrate, in acetone (10 ml.) methylated with diazomethane (0·1g. in 10 ml. ether), the product purified and dried as described in (i) above.

(iv) Methylation with diazomethane followed by hydrolysis with alkali:— The diazomethane methylation product (from (ii) above) was suspended in dilute alkali (25 ml.; 1N) and heated on a boiling water-bath for 5 minutes by which time all the material had dissolved. The alkaline solution was extracted with methyl ethyl ketone to remove traces of unchanged material. The aqueous solution was then acidified with dilute hydrochloric acid (35 ml.; 1N) and extracted with methyl ethyl ketone (100 ml.). The solvent was removed under reduced pressure and the product purified and dried in the usual manner.

Notes

1. Yields of methylation products were usually 90–95 per cent of the original product, losses being accounted for by the purification process.

2. The methylation products are darker in colour than the original material ranging in colour from chocolate-brown to dark-brown.
3. Pure dry ether and acetone were employed in the purification processes.
4. The methylation products are not hydrolysed by dilute mineral acids (5N), even after prolonged heating at 100° C.

(*d*) Reduction with zinc dust and hydrochloric acid

The ether-insoluble material (2g.), dissolved in 15 ml. acetone, was mechanically stirred and 5·0 g. zinc dust and 30 ml. aqueous hydrochloric acid (V/V) added in small amounts over a period of 5 hours, after which the mixture was stirred for an additional 3 hours. Frothing took place during the latter stages of the experiment. The product was then neutralized with solid sodium carbonate and an excess sodium carbonate (2·5g.) added. The suspension was heated at 100° C. for one hour and the precipitated zinc carbonate removed by filtration. The filtrate was acidified when the reduced product was precipitated, the suspension extracted with methyl ethyl ketone and the solvent removed under reduced pressure. The residue (1·5g.) was taken up in a minimum of ethanol (15 ml.) and the product precipitated by the addition of ether. The chromatographic separation of the mixture of reduced product is described under experiment (*g*) below.

(*e*) Oxidation of the reduced product from (*d*) with nitric acid

The mixture of reduced products (1·0g.) was dissolved in concentrated nitric acid (20 ml.; 60 per cent) by heating and the dark-brown solution boiled under reflux for 3 hours. The resultant orange-yellow solution was diluted with water (500 ml.) was neutralized with solid sodium carbonate and then rendered just acid with dilute hydrochloric acid (10 ml.; 1N). The turbid suspension was extracted with methyl ethyl ketone (500 ml.) and the solvent removed under reduced pressure. The yellow residue (0.70g.) was taken up in acetone (20 ml.) filtered and precipitated by the addition of ether. The yellow amorphous product was purified and dried in the usual manner.

Analysis Found: C, 51.2; H, 3.1; N, 4.1.%.

The diazomethane methylation product of this reaction product was prepared in the same manner as described under experiment (*e*) (i) above and the light-brown amorphous product purified and dried in the usual way.

Analysis

Found: OCH_3 23·9 %

(*f*) Decarboxylation in quinoline

The powdered ether-insoluble product (1g.) was brought into a heated suspension of copper powder (1g.) in quinoline (10 ml.) at 210–220° C. over a period of ten minutes whilst stirring with a thermometer. Carbon dioxide was evolved. The temperature was kept constant at 210–220° C. for 1½ hours after which no more gas bubbles were evolved. This mixture was allowed to cool and methyl ethyl ketone (25 ml.) added. The precipitate was filtered, washed with methyl ethyl ketone and extracted with pyridine in a Soxhlet apparatus for 12 hours by which time the extract was colourless and contained no more material. The pyridine was removed under reduced pressure and the dark-brown residue (0·5g.) purified by precipitation with ether from a pyridine solution. The precipitate was washed with ether, suspended in dilute hydrochloric acid (50 ml.; 5 N) and heated on a boiling water-bath. After half an hour the dilute acid was decanted off and the treatment repeated twice to remove adsorbed pyridine. The product was then

washed with boiling distilled water until the filtrate was chloride-free. It was dried by washing first with ethanol and then with ether and dried finally in a high vacuum at 50° C. for 3 hours.

Analysis

Found: C, 66·0.; H, 3·4.; N, 7·5 %.
Atomic ratio: C, 1; H, 0·63; N, 0·098; O, 0·26.

The pure product was methylated with diazomethane as described under (*c*) (i) above except that the methylation was done on a suspension of the decarboxylation product in ether. The methylation product was dried in the usual manner.

Analysis

Found: OCH_3 6·58 %.

(*g*) Chromatographic separation

1. *Preparation of the cellulose adsorbent.* Filter paper was torn into small pieces and digested in water on a boiling water-bath for 8 hours. It was then stirred vigorously with a mechanical stirrer until a fine pulp was obtained. This was poured on a column and washed under suction with water, alcohol and acetone successively.

2. *Chromatographic separation of the ether-insoluble acid mixture.* The mixture (5g.) was dissolved in acetone (200 ml.) and poured on a column of cellulose (70g.) (dry weight) prepared as described under (1) above. A number of brown bands were formed. These were developed and eluted with various eluents as indicated in Table VII.

TABLE VII

Data of chromatographic separation on cellulose

Band	*Colour*	*Eluent*	*Volume of eluent (ml.)*	*Number of fraction*	*Section of column*
1	Dark-brown	(2N) Ammonia	400	(IV and V)*	Top
2	Brown	Water	500	III	
3	Brown	Ethanol	250	II	
		Acetone	500	I	Bottom

* See re-chromatography below. The elution of each fraction was continued until the eluate was colourless. Solvent mixtures attempted for elution of the bands proved unsuccessful.

Re-chromatography

Fraction I. The eluate comprising fraction I was evaporated to a small volume (20 ml.) and poured on a column of cellulose (15g. dry weight) saturated with ether. A dark-brown adsorption band was formed. This band was not affected by ether. The column therefore, was subjected to development and elution of the various fractions in the same manner as was employed for the primary separation given above. Small amounts of fractions II, III and IV were obtained. These were added to the respective fractions from the previous chromatogram. The main fraction, viz. the acetone eluate was evaporated to a small volume (20 ml.) and precipitated by the addition of ether (100 ml.). The light brown amorphous product (2·31g.) was purified and dried in the usual manner.

Analysis Found: C, 50·9; H, 3·0; N, 4·1
$C_{60}H_{40}N_4O_{38}$ requires: C, 50·6; H, 2·8; N, 3·9 %.

Fraction II. This was re-chromatographed on cellulose (5g.) and small amounts of fractions III and IV again obtained together with traces of fraction I. The main eluate in ethanol (200 ml.) was evaporated to a small volume (20 ml.) and precipitated by the addition of ether (10 ml.). The brown amorphous product (0·1g.) was purified by reprecipitation and dried in the usual manner.

Analysis Found: C, 50·0, H, 2·8, N, 3·8
$C_{60}H_{40}N_4O_{38}$ requires: C, 50·6, H, 2·8, N, 3·9 %.

Fraction III. This dark-brown eluate was acidified, extracted with methyl ethyl ketone and the solvent removed under reduced pressure. The residue was taken up in acetone and chromatographed on cellulose (15g. dry weight) as described above. The main eluate was the acetone eluate which was evaporated to a small volume, precipitated by the addition of ether (1g.) and purified and dried in the usual manner.

Analysis Found: C, 54·0; H, 3·25; N, 2·9
$C_{60}H_{40}N_2O_{34}$ requires: C, 53·5; H, 3·0; N, 3·1 %.

Fractions IV and V. The ammonia eluate was acidified when a dark brown amorphous precipitate settled out. This was filtered (1·2g.) and dissolved in acetone (30 ml.). The acetone solution was chromatographed on cellulose (6g. dry weight). As with fraction III above, the extraordinary property was exhibited namely that a fraction which had formerly been strongly adsorbed, could now be eluted with acetone. After elution with acetone (IV) until the eluate was colourless, alcohol and water were poured successively through the column without causing any elution. Ammonia (2N) eluted the rest of the material (fraction V). The products were separated, purified and dried as for the previous fractions. Fraction IV (0·71g.) was a dark-brown amorphous product and fraction V (0·30g.) was still darker brown in colour and also amorphous

Fraction IV: Found: C, 56·5; H, 2·7; N, 3·2
$C_{60}H_{34}N_2O_{31}$ requires: C, 55·7; H, 2·6; N, 3·25 %.
Fraction V: Found: C, 35·8; H, 4·2; N, 3·5
$C_{60}H_{80}N_5O_{70}$ requires: C, 36·2; H, 4·0; N, 3·5 %.

The five fractions were methylated with diazomethane as described under experiment (*c*) (i) above and the products purified and dried in the usual manner. The methylation products were darker in colour than the original products.

Analysis

	Per cent OCH_3
Fraction I	16·5
„ II	18·0
„ III	16·5
„ IV	18·25
„ V	13·5

3. *Chromatographic separation of the mixture of reduced products from experiment (d) above.* The mixture (0·5g.) was dissolved in acetone (25 ml.) and brought on to a column of cellulose (5g., dry weight). The chromatogram was developed and the fractions eluted

with various solvents as indicated in Table VIII. The elution of each fraction was continued until the eluate was colourless and left a negligible residue on evaporation of the solvent.

TABLE VIII

Fraction number	*Eluent*	*Volume of eluent (ml.)*	*Colour of eluate*	*Weight of residue*	*Section of column*
IV	Ammonia (2N)	300	Dark-Brown	Negligible	Top
III	Water	250	Brown	do.	
II	Acetone alcohol (V/V)	300	Brownish-red	0·10g.	
I	Acetone	500	Dark-brown	0·30g.	Bottom

Fractions I and II were rechromatographed on cellulose and the main fractions, viz. the residues from the acetone and the acetone-alcohol eluates respectively were purified and dried in the usual manner to yield dark-brown amorphous solids.

Analysis FractionI. Found: C, 60·8; H, 4·9; N, 2·8 %.
Fraction II. Found: C, 54·7; H, 5·7; N, 1·4 %.

Both fractions I and.II were methylated with diazomethane as described in experiment (*c*) (i) above, and the methylation products purified and dried in the usual manner.

Analyses Fraction I. Found: OCH_3 13·12 %.
Fraction II. Found: OCH_3 16·25 %.

(*b*) **The separation of the neutral ether-insoluble product**

The ether-soluble fraction of the oxidation product (Part I: 215g.) was dissolved in dilute alkali solution (2l; 2N) by heating on a waterbath. The solution was extracted with methyl ethyl ketone until the extract was colourless. The dark brown extract in methyl ethyl ketone (2L) was dried over calcium chloride and the solvent removed under reduced pressure. A dark brown liquid (17g.) was left behind. Ether (250 ml.) was added to this liquid. A dark brown precipitate settled out. This product was filtered and allowed to dry in air. It was purified by repeated precipitation from an acetone solution with ether and dried in the usual manner.

Analysis Found: C, 51·4; H, 3·25; N, 8·75
$C_{80}H_{46}N_9O_{32}$ requires: C, 51·3; H, 3·3; N, 9·0 %.

The product was methylated with diazomethane as described under experiment (*c*) (i) above.

Analysis Found: OCH_3 9·50 %.

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A STUDY OF THE HYDROGEN EXCHANGE IN AQUEOUS SOLUTIONS OF SODIUM FORMATE

by

L. D. C. BOK AND M. D. COHEN

OPSOMMING

By temperature tussen 160 en 215° C. vind 'n uitruiling plaas tussen die waterstowwe van natriumformiaat en die van dié water waarin dit opgelos is. Die reaksie is van die eerste orde en nie grootliks afhanklik van heterogene kataliese nie. Die uitruiling vind heelwat stadiger plaas as in die geval van die ooreenstemmende reaksie van kaliumasetaat. Die energie van aktivering is omtrent 30 kcal. Die meganisme van die reaksie is vermoedlik soortgelyk aan dié van die enolisasie van asetoon.

SUMMARY

At temperatures between 160 and 215° C. an exchange takes place between the hydrogens of sodium formate and those of the water in which it is dissolved. The reaction is of the first order, and not appreciably dependent on heterogeneous catalysis. The exchange takes place much slower than in the case of the corresponding reaction of potassium acetate. The energy of activation is about 30 k. cal. The mechanism of the reaction is considered similar to that of the enolization of acetone.

INTRODUCTION

In general, all hydrogen atoms attached to oxygen, nitrogen, sulphur, or halogen atoms are exchanged rapidly with the deuterium of heavy water, the exchange proceeding until statistical equilibrium is reached.[1,2]

On the other hand, hydrogen atoms attached directly to carbon are only exchanged under the following special circumstances:—

(i) Attack by deuterium atoms formed from D_2 by the action of heat[3], electrical discharge,[4] or excited mercury atoms.[5]
(ii) The presence of certain strong acids, e.g., D_2SO_4[6].
(iii) The presence of a solid catalyst, usually one of the transition metals which also facilitate hydrogenation.[7]
(iv) The hydrogen of the substance considered is mobile due to some special structural feature of the molecule.[8]

The exchange between heavy water and the ions of organic acids falls into the last class. In all the saturated fatty acids so far investigated only the alpha-hydrogen atoms have been exchangeable. This immediately suggests that the alpha-hydrogen has a certain mobility, and it becomes of interest to know what effect the adjacent groups of the molecule have on this mobility. A comprehensive study has been made of the exchange of acetic acid, and acetates, with heavy water.[9] A certain amount of work has been carried out also on propionic and higher acids.[10] In the case of the first member of the homologous series most workers had either stated that there was no exchange,[11,12] or found that the exchange was negligibly slow.[13] No experiments had been carried out above 100° C. To obtain a more complete picture of the exchange with organic acids it was thus necessary to carry out an investigation on formates in a temperature range at which the exchange becomes measurable. The results should throw some light also on the structure of the formate ion, about which there has been some divergence of opinion.

Aqueous solutions of sodium formate of known normality were kept at the required temperature in sealed tubes for a fixed time. The solvent water was then distilled off, and the dried formate burnt in oxygen. The water resulting from the combustion was collected and its deuterium oxide content determined. The exchange was followed in both directions; i.e., "forward", using "light" sodium formate and heavy water, and "back", using deuterated sodium formate and ordinary water.

The results given in Tables I and II were obtained.

TABLE I

Results for the forward exchange

	Temp. °*C.*	*Normality*	*Percentage* D_2O *after time t*	*Time t hours*	*Velocity constant k* (*hours* $^{-1}$)
	160·5	4·1	20	168·0	·00133
		4·8	15	168·0	·00097
	,,	4·6	18	168·0	·00118
	,,	5·4	25	352·0	·00082
	,,	5·4	43	352·0	·00160
	,,	6·6	36	352·0	·00127
Mean	160·5				·00119
	183·0	0·6	7	6·25	·00737
	,,	4·8	9	12·0	·00788
	,,	7·5	14	16·1	·00932
	,,	5·5	26	16·2	·0185
	,,	0·9	10	20·25	·00514
	,,	5·0	6	24·0	·00254
	,,	9·6	14	32·1	·00468
	,,	1·6	16	43·75	·00399
	,,	1·6	16	43·75	·00399
	,,	5·3	16·5	44·0	·00465
	,,	6·1	21·5	57·5	·00418
	,,	4·1	25	57·5	·00496
	,,	4·2	20	86·0	·00257
Mean	183·0				·00510
	211·0	5·0	8	4·0	·0216
	,,	5·0	18·5	8·58	·0237
	,,	5·0	44	14·12	·0411
	,,	5·0	46	19·67	·0360
Mean	211·0				·0306
	212·3	2·4	14	6·47	·0232
	,,	5·3	53	18·6	·0407
	,,	4·2	57·5	18·7	·0457
	,,	4·0	42	18·8	
	,,	4·2	55	20·0	·0388
	,,	4·2	58	21·05	·0411
	,,	3·8	52	21·8	·0336
	,,	11·8	71	54·25	·0228
	,,	8·3	84	68·5	·0255
	,,	12·1	80	94·0	·0169
Mean	212·3				·0320
	214·0	3·3	52	19·0	·0386
	,,	2·9	58	19·0	·0439
	,,	3·0	66	19·0	·0568
Mean	214·0				·0464

TABLE II

Results for the back exchange

	Temp. °C.	*Normality*	*Percentage* D_2O *initial*	*after time t*	*Time t hours*	*Velocity constant k* (*hours*$^{-1}$)
Mean	179·0	1·7	84	36	65·5	(·0129
	,,	3·7	,,	56	65·5	·00670
	,,	2·3	,,	56	65·5	·00670
	,,	2·7	,,	52	68·0	·00708
	,,	4·6	,,	52	68·0	·00708
	,,	4·2	,,	54	68·0	·00650
	,,	2·5	,,	54	68·0	·00650
	,,	0·9	,,	50	68·0	·00765
Mean	179·0					·00689
	195·0	3·1	80	52	16·0	·0269
	,,	2·8	,,	52	16·0	·0269
	,,	2·3	,,	52	16·0	·0269
	,,	2·1	,,	44	29·0	·0206
	,,	1·7	,,	44	29·0	·0206
	,,	2·8	,,	23·5	41·0	·0298
	,,	2·0	,,	25·5	48·0	·0273
Mean	195·0					·0256
	208·2	3·9	71	26	16·0	·0618
	,,	2·6	,,	26	16·0	·0618
	,,	1·3	,,	26	16·0	·0618
	,,	1·2	,,	15	24·0	·0645
	,,	1·3	,,	15	24·0	·0645
	,,	2·2	,,	15	26·0	·0597
	,,	1·4	,,	15	26·0	·0597
Mean	208·2					·0619

The reaction velocity constants k were calculated on the assumption that the reaction was of first order, i.e.:

$$k = \frac{1}{t} \ln \frac{c_o}{c_t}$$

where c_o and c_t are the percentages of H_2O (D_2O) in the water of combustion obtained from samples reacted for times t = O and t respectively.

CONCLUSION

1. A slow exchange definitely does occur.

2. The reaction is of first order, since the velocity is independent of the formate concentration. Due to limitations in the accuracy of the method, differences in the amount of exchange were in some cases found in experiments which were parallel except for slight variations in the concentration of the formate, but these differences were never systematic. A large number of the experiments show the same amount of exchange after the same length of time at the same temperature, even though differences in concentration did exist.

3. The reaction is not appreciably subject to hetergeneous catalysis. This was shown by carrying out parallel experiments with and without the addition of powdered glass. No variation outside the limits of the experimental accuracy was found. (See experiments 14 and 15, Table I.) (cf. Small and Wolfenden.[13])

4. The rate of exchange is considerably slower than that with potassium acetate under similar conditions. (cf. Bok and Geib.[9])

5. The back exchange takes place about 1·7 times as fast as the forward exchange.

6. The activation energy E for the forward and for the reverse reactions is 30 k. cal., and the temperature independent factor A is — 10. These constants were calculated from the expression:

$$k\ (sec^{-1}) = 10^{A}.\ e^{-E/RT}.$$

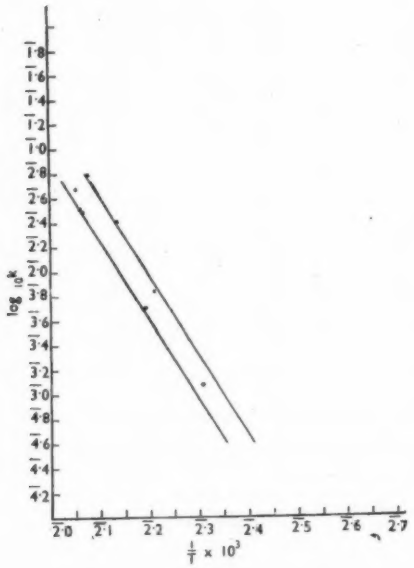


FIG. 1.

The temperature dependence of the reaction velocity is given in Figure 1, in which $\log_{10}$ of the average value of k at the different temperatures has been plotted against the reciprocal of the absolute temperature.

DISCUSSION

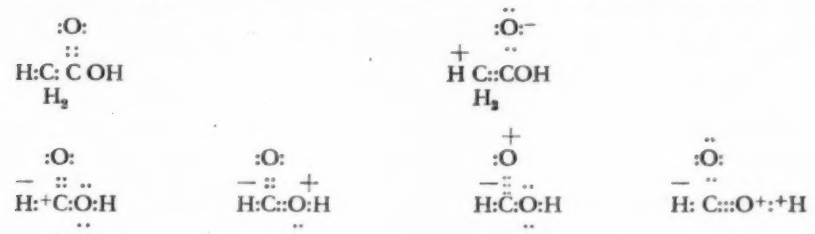
The conditions appear to be very similar to those of the previously observed exchange in acetate solutions without any additions.

Since the concentration of hydroxyl ions formed by hydrolysis is proportional to the root of the formate ion concentration and since no dependence of the reaction velocity on the formate ion concentration was found, the principal reaction cannot be one between formate ions and hydroxyl ions. This also means that formate ions are not important as

catalysts for the exchange. The reaction is thus either one between formate ions and undissociated water molecules, or between hydroxyl ions and undissociated formic acid. Both of these cases would give the same concentration dependence, as hydrolysis takes place according to the equation

$$Na^+ + HCOO^- + H_2O = Na^+ + HCOOH + OH^-.$$

The following resonance forms of acetic and formic acids have been postulated[19]



Whereas in the case of acetic acid the alpha-hydrogen atom tends to become positively charged in a "no-bond" condition, the hydrogen atom in formic acid is apt to be negatively charged. Thus the acetic alpha-hydrogen would be more easily removed in a proton transfer reaction than the formic acid hydrogen despite any possible tendency to hydride ion formation.

It was considered probable that the hydrogen exchange in the case of acetate occurred through a mechanism similar to that suggested for the enolization of acetone.[9, 14] For the base induced ketone halogenation, racemization and deuterium exchange the rate determining step has been taken to be the proton transfer

$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + B = H_3C-\overset{O}{\overset{\|}{C}}-CH_2^- + BH \qquad (1)$$

A similar scheme for the mechanism of the exchange in solutions of light sodium formate in heavy water, if the reation were between formate ions and water molecules, would be the proton transfer

$$O-\overset{O}{\overset{\|}{C}}-H + D_2O = {}^-O-\overset{O}{\overset{\|}{C}}{}^- + HD_2O^+ \qquad (2)$$

followed by the deuteron transfer

$${}^-O-\overset{O}{\overset{\|}{C}}{}^- + D_2O = {}^-O-\overset{O}{\overset{\|}{C}}-D + OD^- \qquad (3)$$

If the reaction were one between undissociated formic acid molecules and deuteroxyl ions the scheme would be

$$D-O-\overset{O}{\overset{\|}{C}}-H + OD^- = D-O-\overset{O}{\overset{\|}{C}}{}^- + HDO \qquad (4)$$

and

$$D-O-\overset{O}{\overset{\|}{C}}{}^- + D_2O = D-O-\overset{O}{\overset{\|}{C}}-D + OD^- \qquad (5)$$

From resonance considerations an acetate ion, or acetic acid molecule, would be expected to show a greater tendency than a formate ion, or formic acid molecule, to give off a proton in the reaction corresponding to (2) or (4). This agrees with the result that the hydrogen exchange in solutions of sodium formate without any additions has been found to be slower than the corresponding exchange with acetate.

In the case of the formate, however, the reaction of deuterated formate with light water appears to proceed more rapidly than the reaction of light formate with heavy water. Since, in general, the same reaction should be slower when involving a deuteron transfer than when involving a proton transfer, this effect may be explained on the basis that whereas with acetate the reaction corresponding to (2) or (4) is rate determining, in the case of formate it is the second step (3) or (5) which is the slower of the two.

The formation of the ion is taken to be the condition for the base induced deuterium exchange, and the further formation of an enol form would not be anything more than an unimportant by-path into which a fraction of the reacting substance would be temporarily transformed. If, however, a portion of the reaction were acid induced, then the formation of enol would be a prerequisite and might take place along the lines

$$D-O-\underset{\displaystyle H}{\underset{|}{C}}=O + DA = D-O-\underset{\displaystyle H}{\underset{|}{C}}-O-D + A^- \quad \text{.....(6)}$$

$$D-O-\underset{\displaystyle H}{\underset{|}{C}}-O-D + A^- = D-O-C-O-D + HA \quad \text{.....(7)}$$

The presence in formic acid of at least traces of material of formula $C(OH)_2$ has been considered probable by Davis and Green[15] who suggested that the interaction of bromine and anhydrous formic acid produces an intermediate substance, evidently capable of existence only in the presence of free Br_2, which is probably $Br_2C(OH)_2$.

Miklukhin[12] criticised Davis and Green's conclusion on the grounds that he found no exchange between the hydrogen attached to carbon in formic acid and the deuterium of heavy water. Since, however, a measurable exchange does take place at higher temperatures this criticism largely falls away.

Sarkar and Rây[16] have suggested that the radical difference in properties between formic acid and the higher homologous acids is explained by a fundamentally different structure of the formate ion in solution. The structural difference suggested was that in formic acid the ionizable hydrogen is the hydrogen attached to the carbon atom. The fact that the hydrogen exchange between formates and heavy water is extremely slow provides strong evidence against the proposal of Sarkar and Rây. Nevertheless, their arguments would at least suggest the existence of traces of an enol form.

If part of the observed exchange were to take place according to equations (6) and (7), then since the OH^- concentration and therefore the H^+ concentration are dependent on the formate ion concentration, the observed independence of the rate on the formate concentration means that (6) cannot be the rate determining step. Further, as reaction (6) is a proton or deuteron transfer reaction it would be expected that if this were the rate determining step the reaction in heavy water would be slower than the reaction in light water. Since this was not found experimentally, the rate should rather be determined by reaction (7). Hammett[17] advances arguments to show that the reaction corresponding to (7) is rate determining in the case of the acid induced enolization.

In the case of acetone the halogenation gave evidence supporting the mechanism suggested. The bromination of formic acid was followed kinetically by Hammick,

Hutchinson and Snell[18] who found the reaction to be bimolecular and retarded by the presence of HBr. The reaction was

$$HCOOH + Br_2 = CO_2 + 2HBr.$$

As this reaction leads to the complete break-up of the formic acid molecule, there would be very little resemblance between its mechanism and that of the hydrogen exchange.

EXPERIMENTAL

Forward exchange

Sodium formate was dried under high vacuum and about 0·05g. weighed out into a 8 mm. internal diameter Monax-glass tube. Approximately 0·15 g. of heavy water was then "weighed in", and the tube was sealed and immersed in glycerine maintained at a constant temperature in a thermostat. In the earlier experiments a "boiling-liquid thermostat" was used, which consisted essentially of two concentric copper cylinders, the inner one containing glycerine and the outer a liquid boiling under reflux. Liquids used were aniline and nitrobenzene. In later experiments copper tubes containing glycerine were immersed in a well stirred oil-bath maintained at constant temperature by an immersion heater controlled by an electric relay actuated by a toluene-type regulator filled with mercury. The experiments for which the temperature is given as 160·5° C. had their temperature less rigidly controlled, as at this temperature the sealed tubes were merely left in a laboratory electric drying oven.

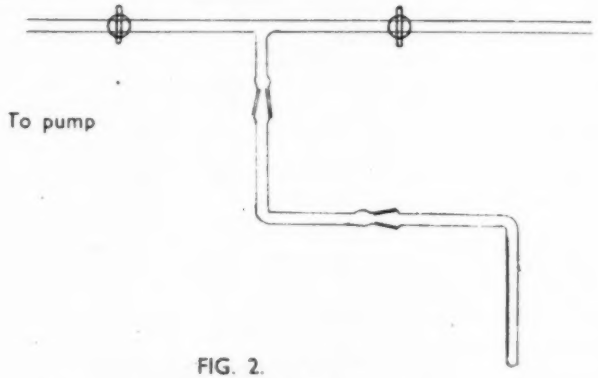


FIG. 2.

When the sealed tubes had been maintained at the reaction temperature for the required time, they were removed, sealed on to a ground-glass joint and connected through a moveable arm (Fig. 2) to a high vacuum system (3×10^{-4} mm. Hg.). This arrangement allowed the tube to be moved and shaken while under vacuum, so that the water distilled off rapidly. After drying at room temperature the tube was evacuated for a further hour at 100° C. to remove absorbed water. The inch or so of tube containing the dried formate was sealed off under vacuum and retained for combustion.

Back exchange

Deuterated sodium formate was prepared by dissolving about 1 g. dried light formate in about 1 ml. of heavy water in a Monax-glass tube which was thereupon sealed and maintained at 210° C. for 2–3 days. The tube was then opened and dried as in the for-

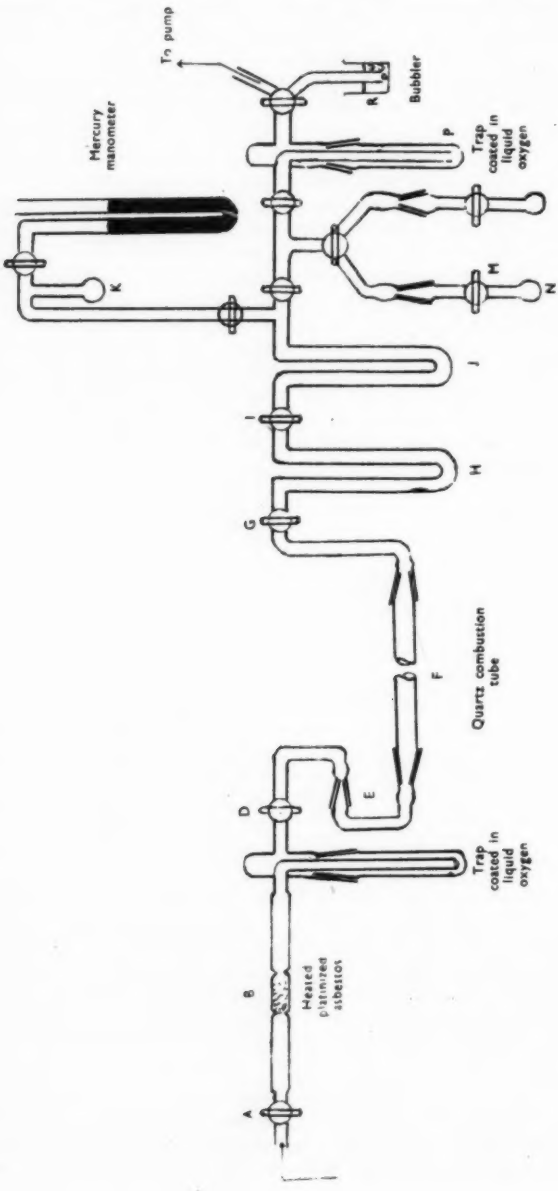

To pump
Mercury manometer
Bubbler
R
P
Trap coated in liquid oxygen
K
M
N
Sample tubes
J
I
H
G
F
Quartz combustion tube
E
D
Trap coated in liquid oxygen
B
Heated platinized asbestos
A

FIG. 1.

ward exchange. The residual, partly deuterated, sodium formate was the starting material for the back exchange.

The dried deuterated formate was divided up into several portions of about 0·05 g. each, of which one was retained for direct combustion and analysis. The others were dissolved in approximately 0·15 g. of ordinary distilled water and treated further as in the forward exchange, until there remained dried samples of formate ready for combustion

Combustion

The determination of the deuterium content of the dried formate required the prior conversion of the hydrogen to water. This was achieved by heating the sample in a stream of oxygen in the combustion apparatus. The combustion train was so arranged that it could be evacuated to high vacuum. This allowed the apparatus and enclosed formate to be thoroughly dried before the combustion was started, and ,after the completion of the combustion, allowed the water formed to be distilled into sample tubes.

The apparatus is shown diagramatically in Fig. 3. Oxygen from a cylinder was freed of foreign gases, in particular hydrogen and hydrocarbons, by passing it over heated platinized asbestos (B). The oxidized products so obtained were frozen out in a trap cooled in liquid oxygen (C), and the pure oxygen entered the quartz combustion tube (F) which contained in order (i) the section of the Monax-glass tube containing the dried formate, which had been cut open and was allowed to rest on a piece of platinum foil to avoid fusion of the glass to the quartz, (ii) a platinum foil to act as catalyst for the conversion of hydrogen and carbon to water and carbon dioxide, respectively, and (iii) a silver spiral which served to retain any N, S, or halogen compounds. After leaving the quartz combustion tube the gas flowed through a U-tube (H) cooled in dry-ice/acetone, where the water of combustion was frozen out. The last traces of water were brought into this U-tube after the completion of the combustion by cutting off the oxygen supply and evacuating the apparatus, with the cooling mixture still in place around (H). After a vacuum had been attained the cooling mixture was transferred from U-tube (H) to U-tube (I). This caused the water to distil across from one U-tube to the other, and partly freed it from dissolved CO_2. After a vacuum had been reached in the system, it was then closed to the pump, and the cooling mixture transferred to the bulb of the sample-tube (M), and thus all the water was distilled into it. The stopcock of the sample-tube was then closed, after which the tube was disconnected at the ground-glass joint and stored until measurements could be carried out. The storage period was, as far as possible, not more than a few days.

Measurement

The deuterium content of the samples of water was determined by the method of P. Harteck, which is based on the comparison of the sublimation pressure at — 21° C. of ice from the water of the unknown sample with the sublimation pressure at the same temperature of ice from pure H_2O and D_2O respectively. These pressures are compared by means of a thermal conductivity cell of a type first used by Bonhoeffer and Harteck[20] to analyse ortho-para hydrogen mixtures, and adapted by Farkas and Farkas[21] to estimate the amount of heavy isotope in hydrogen gas. The method was then applied by Harteck[22] to the determination of the deuterium content of small quantities of water. The actual cell used in this investigation was of simplified design, which made it easy to construct. It is illustrated in the diagram of the measuring section (Fig. 4). Its length was 18 cm. and its diameter 1·5 cm. The platinum wire of diameter 0·002 inches had a total resistance of about 9 ohm.

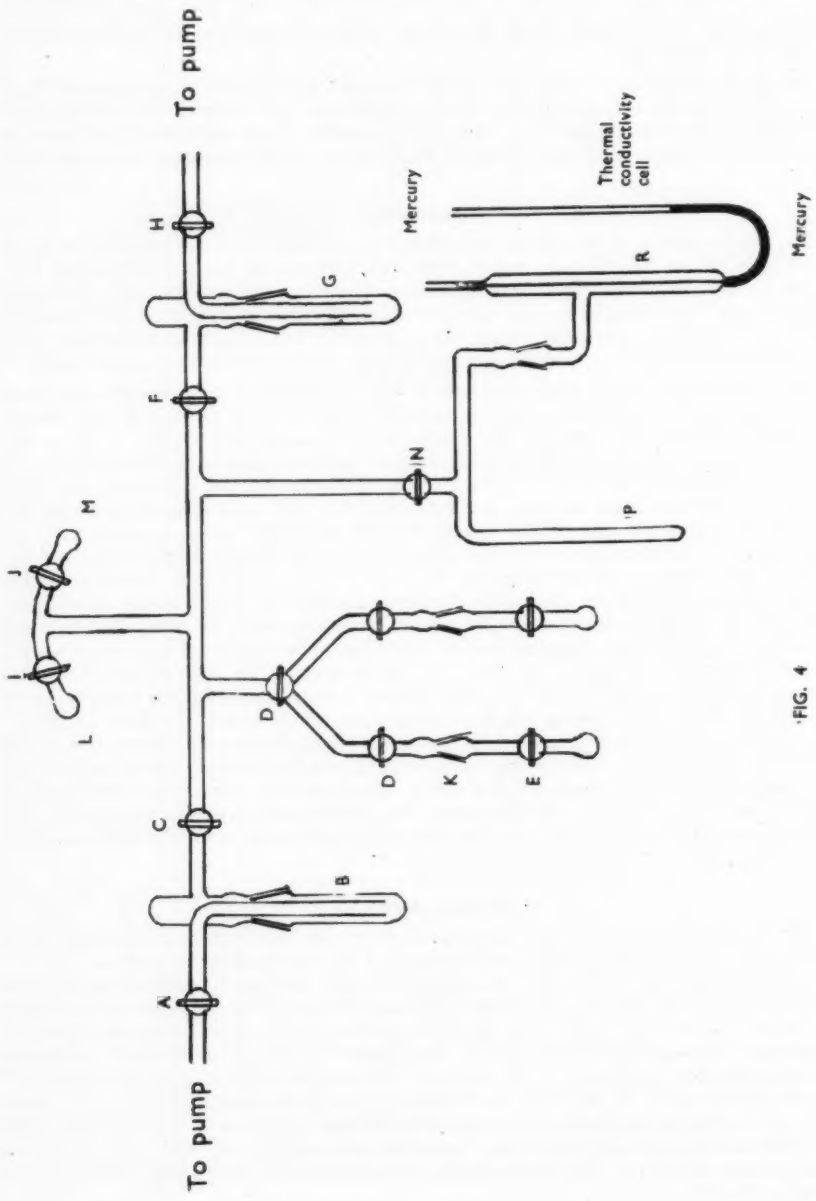

To pump
To pump
Thermal conductivity cell
Mercury
Mercury
A
B
C
D
D
E
F
G
H
I
J
K
L
M
N
P
R

FIG. 4

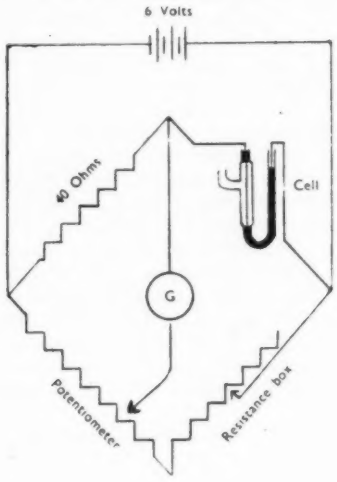
In the measuring section (see Fig. 4) a side-arm tube (P) was attached adjacent to the thermal conductivity cell (R). The side-arm tube was maintained at a constant temperature in the vicinity of — 21° C. (at this temperature a suitable difference exists between the sublimation pressures of H_2O and D_2O). Before any determinations could be made, the bulbs L and M had to be filled with light and heavy water, respectively, as these were used as reference standards. With vacuum (3 x 10^{-4} mm. Hg.) in the apparatus, the reference water was introduced from a tube attached to the ground-glass joint K, and frozen out in the trap G by cooling the latter in dry-ice/acetone. This water was then distilled at least four times between the traps B and G in order to remove any dissolved air or carbon dioxide. When distilling from B to G, for example, the stopcock A was kept closed and stopcock H, leading to the pump, open. To prevent any fractionation during these distillations, it was important that all the water was distilled over. The reference water was finally distilled into its appropriate bulb by having the appartus evacuated while the water was frozen out in one of the traps, and then closing stopcocks A and H and transferring the cooling mixture to the bulb whose stopcock was open. Once the stopcock was closed, the reference water could be stored in its bulb until required for determinations. Immediately prior to use, the bulbs containing the reference standards were cooled in dry-ice/acetone and evacuated, so as to remove any air that might have leaked in while standing.

The sample tube containing the water whose deuterium content was to be established, was attached to the ground-glass joint K, and the water was distilled into the apparatus and collected in one of the traps. It was then distilled between the two traps B and G as in the case of the reference water. It was stored in the trap B until required in the determination.

After the measuring section had been evacuated to 3 x 10^{-4} mm. Hg, the space between the stopcocks C-I-J-F-N-P was filled with the vapour of the sample or reference water by opening the appropriate stopcock for 15 seconds. Thus a definite volume (about 40 c.c.) of water vapour at the saturation pressure at room temperature (about 0·5 mg. of water) was admitted for each reading. This avoided difficulties due to a difference in composition, varying with the amount of substance present, between the solid and vapour phases in the tube (P) at — 21° C. resulting from the difference in saturation pressures of light and heavy ice respectively. The vapour in the space C-I-J-F-N-P was then allowed to flow into the evacuated section containing the thermal conductivity cell and side-arm attachment by opening stopcock (N) for 15 seconds. Ice then formed in the side-arm at — 21° C. and exerted its sublimation pressure. The walls of the thermal conductivity cell were kept immersed in melting ice which kept them at a constant temperature. A potential was then applied to the ends of the platinum wire, and after a further 90 seconds the resistance of the wire was determined. Thereafter the current to the wire was switched off and the water vapour was removed from the measuring section by opening it to the pump and evacuating for one minute.

Times of opening stopcocks, of applying current, and of evacuation were standardized to ensure that the temperature of the platinum wire approached equilibrium to the same extent on all occasions, to obtain the same amount of evacuation before every reading, and to allow for any small constant leakage into the measuring space while waiting. When a voltage was applied to the platinum wire, the heat lost was dependent upon (i) the dimensions of the thermal conductivity cell, (ii) the applied voltage, (iii) the temperature of the outer cell walls, and particularly, (iv) at low enough pressure was proportional to the pressure of the vapour present (neglecting the difference in specific heats of the water of different isotopic content). As the first three factors were kept constant, only the vapour pressure varied. Thus the temperature and therefore the resistance of the platinum wire varied as the vapour pressure in the cell varied.

The electrical circuit



Electrical circuit

FIG. 5

This included a potentiometer, with sliding centre contact, whose total resistance was 100,000 ohm, a 10,000 ohm resistance box used as a variable resistance, a four-ohm coil resistance, and the thermal conductivity cell. The null point instrument was a mirrored d'Arsonval galvanometer with lamp and scale, with resistance 584 ohm and sensitivity 1,330 mm. per microamp (at 1 metre).

The stability of the applied voltage was of major importance. A heavy duty 6-volt accumulator was employed. After being fully charged the "battery" was discharged for some hours through a 1,000 ohm resistance to stabilize the voltage before using it for measurements.

As it was only necessary to compare the resistances of the wire when surrounded by reference waters and samples, the actual resistance in ohms was not required, and it was sufficient to note the reading of the resistance box, the potentiometer setting being kept constant. In measurements, the potentiometer was first adjusted by introducing light water into the thermal conductivity cell, keeping the resistance box set at 2,000 ohm and varying the potentiometer until no deflexion of the galvanometer was obtained. When at least two consecutive readings of the potentiometer for no galvanometer deflexion were the same, heavy water replaced the light water in the thermal conductivity cell and the resistance box was now varied while the potentiometer was kept constant. The setting of the latter was then kept constant during the rest of the readings. Following at least two constant consecutive readings of the resistance box for no deflexion of the galvanometer, the heavy water was followed by light water, and this was followed in turn by the samples whose deuterium content was to be determined. Finally, the readings for the

light and heavy waters were repeated, so that any drift in the reference water standards could be noted and allowed for. The D_2O content of the samples was then established by means of a calibration curve.

Constant temperatures in the vicinity of — 21° C.

It was necessary for the temperature around tube (P) to be kept constant somewhere in the vicinity of — 21° C.

Methyl chloride boils at — 24° C., so that a possible method appeared to be the immersion of (P) in boiling methyl chloride. Methyl chloride was prepared at first from PCl_3 and CH_3OH, and later from $H_2SO_4 + NaCl + CH_3OH$, being passed through a soda-lime tower and a calcium chloride tower, and then condensed with dry-ice/acetone. It was distilled into a glass mantle surrounding tube (P), and allowed to boil there under reflux from a side tube passing through dry-ice/acetone, the side-tube being attached at the upper end of the surrounding mantle. Using this method a small but distinct difference was found between the readings for light and heavy water, but the readings showed a tendency to drift, which was probably due to unsteady boiling of the methyl chloride. Difficulty was also experienced in storing this substance, so that it had to be prepared afresh for each day's measurement.

The use of boiling methyl chloride was abandoned in favour of the use of an ice/salt eutectic. For this method tube (P) was surrounded by an aluminium block, 16 cm. long and 5 cm. in diameter. A saturated aqueous solution of sodium chloride was placed in a Dewar flask and thoroughly stirred while liquid oxygen was blown on to its surface. This was continued until the material in the Dewar flask was of a thick consistency due to the formation of some eutectic. In the meanwhile the aluminium block was cooled to — 180° C. by immersion in liquid oxygen. The liquid oxygen around the aluminium block was then rapidly replaced by the partly formed eutectic mixture in the Dewar flask, when a thick adherent layer of cryohydrate formed on the surface of the aluminium. After about half-an-hour the temperature became constant and was maintained for about six hours when pure salt and a good Dewar flask were used.

Attempts to form a suitable eutectic by the use of dry-ice proved unsuccessful.

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THE RATE OF HYDROGEN EXCHANGE IN AQUEOUS SOLUTIONS OF AMINO-ACETIC ACID

by

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OPSOMMING

Die waterstofione van amino-asynsuur en dié van die water waarin dit opgelos is word met 'n meetbare snelheid uitgeruil by temperature tussen 140 en 160° C. Die reaksie is van die eerste orde, en baie vinniger as die ooreenstemmende reaksie van kaliumasetaat. Die energie van aktivering is ongeveer 20 k. cal. 'n Meganisme word voorgestel soortgelyk aan dié van die enolisasie van asetoon.

SUMMARY

The hydrogens of amino-acetic acid and those of the water in which it is dissolved are exchanged with a measurable rate at temperatures between 140 and 160° C. The reaction is of the first order, and much faster than the corresponding reaction of potassium acetate. The energy of activation is about 20 k. cal. A mechanism is proposed similar to that for the enolization of acetone.

INTRODUCTION

The rate of exchange of hydrogen attached to a carbon atom, rendered measurable by the presence of a — COOH group as an immediate neighbour, is further influenced by the nature of other atoms or radicals attached to the same carbon atom. Thus the kinetics of the hydrogen exchange have already been investigated in the case of potassium acetate[1] and sodium formate.[2] There is a significant difference in the rates for these two compounds.

In 1937 an orientating result for the exchange of hydrogens in the $-CH_2-$ group in amino-acetic acid was reported by Günther,[3] and mentioned in a table given by Bonhoeffer[4]. To find the effect of the $-NH_2$ group on the exchangeability of hydrogen attached to the alpha-carbon of a saturated fatty acid, it was necessary to study the kinetics of this process, and thus the present investigation was undertaken.

Exchange experiments were carried out at 140, 150, and 160° C. The exchange was followed in both directions, i.e., "forward", using amino-acetic acid and "heavy" water, and "back", using deuterated amino-acetic acid and light water.

RESULTS

The results given in Tables I and II were obtained.

Aqueous solutions of amino-acetic acid in sealed pyrex tubes were kept at the required temperature for the times mentioned in the Table. After this, in the case of the forward exchange, as the investigation concerned only hydrogen atoms attached to carbon, it was necessary to distinguish any exchange in the $-CH_2-$ group from exchange in the $-COOH$ and $-NH$ groups whose hydrogens are easily exchangeable. This was done by distilling off the solvent water, and dissolving the deuterated amino-acetic acid in light water at room temperature, and then again distilling off the water. The dried amino-acetic acid was then combusted in oxygen, and the D_2O content of the water formed was determined. For back exchange a portion of the deuterated amino-acetic acid obtained in the above manner, and whose deuterium content was determined after replacing the easily exchangeable hydrogens with protium, was dissolved in light water and kept at the elevated temperature for a fixed time, and further treated as in the case of forward exchange.

TABLE I

Results for the forward exchange

	Temp. °C.	*Conc.* (g./cm.³)	*Percentage D_2O after time t. (With H in —COOH group)*	*Time t hours*	*Velocity constant k* $(hours)^{-1}$
	140	0·133	11·7	2·0	0·173
	,,	0·238	13·4	2·23	0·183
	,,	0·152	20·0	4·0	0·173
	,,	0·336	20·6	4·17	0·174
	,,	0·192	31·0	6·0	0·249
	,,	0·249	25·4	6·17	0·163
	,,	0·205	32·2	10·0	0·164
	,,	0·192	34·7	16·0	0·126
Mean	140				0·176
	150	0·269	17·6	2·0	0·290
	,,	0·193	22·8	2·96	0·285
	,,	0·210	27·7	4·0	0·295
	,,	0·467	30·7	4·65	0·314
	,,	0·192	24·6	5·0	0·191
	,,	0·187	33·9	6·0	0·313
	,,	0·237	34·2	7·0	0·276
	,,	0·273	39·0	12·0	0·307
	,,	0·275	39·3	13·23	0·306
Mean	150				0·298
	160	0·176	11·1	1·0	0·325
	,,	0·195	22·1	1·50	0·536
	,,	0·193	24·2	2·0	0·466
	,,	0·218	31·0	3·0	0·497
	,,	0·324	31·5	3·3	0·470
	,,	0·163	33·3	3·5	0·511
	,,	0·241	37·5	4·13	0·671
	,,	0·322	34·4	4·5	0·437
	,,	0·174	35·6	4·52	0·489
	,,	0·171	36·8	5·0	0·505
	,,	0·206	36·6	5·63	0·438
	,,	0·178	36·7	7·0	0·357
	,,	0·237	39·4	7·93	0·528
	,,	0·186	39·8	8·0	0·664
Mean	160				0·493
Mean					

The reaction velocity constants k were calculated from the first order equation $k = 1/t \ln c_o/c_t$. In calculating results for the forward exchange, to allow for the fact that the investigation concerns only 40 per cent of the hydrogens in the molecule, namely those in the $-CH_2-$ group, c_o was taken to be 40 per cent. H_2O, and c_t represented the percentage of protium oxide in the water of combustion minus 60 per cent. For the back exchange c_o represented the percentage D_2O found in the water of combustion from the deuterated amino-acetic acid samples with easily exchangeable hydrogens replaced with protium, while c_t represented the percentage D_2O in the water of combustion from portions of these samples which had been t hours at the elevated temperature while dissolved in light water.

TABLE II

Results for the back exchange

	Temp. °*C.*	*Conc.* (*g./cm.*³)	*Percentage* D_2O *initial*	*After time t*	*Time t hours*	*Velocity constant k* (*hours*)$^{-1}$
	140	0·204	35·6	27·8	3·23	0·0766
	,,	0·185	35·6	25·2	4·00	0·0864
	,,	0·138	36·0	25·2	4·92	0·0725
	,,	0·137	36·0	23·0	5·91	0·0759
Mean	140					0·0779
	150	0·163	26·2	22·9	1·0	0·135
	,,	0·148	27·8	20·9	2·11	0·135
	,,	0·165	27·8	18·3	3·11	0·134
	,,	0·158	26·2	10·9	6·05	0·145
Mean	150					0·137
	160	0·132	38·3	24·2	2·0	0·230
	,,	0·232	36·5	19·0	2·6	0·251
	,,	0·147	38·3	15·6	4·1	0·219
	,,	0·136	36·5	12·2	4·75	0·231
Mean	160					0·233

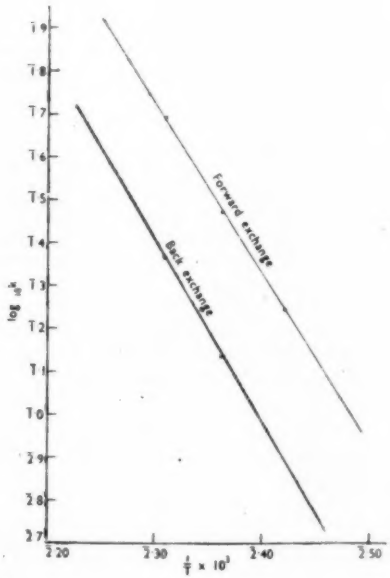

FIG. 1.

The temperature dependence of the reaction velocity is given in Fig. 1, in which $\log_{10}$ of the average value of k at the different temperatures has been plotted against the reciprocal of the absolute temperature. The activation energy calculated from the slope of the lines is just under 20 k. cal., while the temperature independent factor is approximately 13.

DISCUSSION

It appears that the hydrogens in the $-CH_2-$ group do definitely exchange with those of the solvent water at temperatures within the range 140–160° C. The reaction is of first order since the velocity is independent of the amino-acetic acid concentration. (Compare, e.g., experiments 3 and 4, Table I.) The exchange takes place much more rapidly than the corresponding exchange for potassium acetate[1], which in turn is faster than that of sodium formate.[2] This may be attributed to the presence of the $-NH_2$ group in the molecule. Without taking into account any possible effect of the pH of the solution, the comparison is given in Table III, which gives the approximate times of half change of the three substances for the forward reaction at 160° C.

TABLE III

Substance	*Time of half change (hours)*
Amino-acetic ...	1·4
Potassium acetate	40
Sodium formate ...	800

The forward exchange for amino-acetic acid is about twice as fast as the back exchange, which was the same in the case of potassium acetate. In the case of sodium formate the back exchange was found to be 1·7 times as fast as the forward exchange.

In general, conditions appear to be similar to those found in the previously observed hydrogen exchanges between solvent water, and formate and acetate respectively. It seems likely that the mechanism is similar.

Since the reaction rate was not found to be dependent on the concentration of the amino-acetate ion, it follows for the same reasons as those given in the previous paper that the main reaction cannot be one between hydroxyl and amino-acetate ions, and the latter cannot act as a catalyst for the reaction. The reaction, therefore, is probably one between amino-acetate ions and undissociated water molecules, or between hydroxyl ions and undissociated amino-acetic acid.

The hydrogen exchange with acetate and formate was considered to occur through a mechanism similar to that suggested for the enolization of acetone. A possible mechanism along these lines, if the reaction is one between amino-acetate ions and water molecules, would involve the proton transfer

$$O-C(=O)-CH_2-NH_3^+ + D_2O = O-C(=O)-\overline{C}H-NH_3^+ + HD_2O^+ \quad (1)$$

followed by the deuteron transfer

$$O-C(=O)-\overline{C}H-NH_3^+ + D_2O = O-C(=O)-CH(D)-NH_3^+ + OD^- \quad (2)$$

If the reaction is one between undissociated amino-acetic acid and deuteroxyl ions, the mechanism might be

$$H_2N-CH_2-COOD + \overline{O}D- = H_2N-\overline{C}H-COOD + HDO \quad \text{.....(3)}$$

followed by

$$H_2N-\overline{C}H-COOD + D_2O = H_2N-CDH-COOD + OD^- \quad \text{.....(4)}$$

In this case it was found that the forward exchange was about twice as rapid as the back exchange. Since a reaction involving a proton transfer is normally more rapid than one involving a deuteron transfer, step (1) or (3) is probably the rate determining one.

EXPERIMENTAL

The same experimental methods were used as those reported in the previous paper.[2] To keep samples at the required temperature a thermostatically controlled oil-bath was used throughout. The sample tubes were placed in a covering of wire gauze and immersed directly in the oil. The sample tubes contained about 0·1 g. of dried amino-acetic acid and about 0·5 g. of heavy water. An additional precaution regarding the stability of the applied voltage in the electrical circuit, was the use of two heavy-duty 6-volt accumulators placed in parallel, and having both in a box surrounded with straw in a larger box, so as to keep them at constant temperature. For all D_2O determinations the temperature of the side-arm tube adjoining the thermal-conductivity cell was maintained at $-$ 21° C. by the use of an ice-salt eutectic.

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STUDIES ON ISOTOPES

PART I. THE ISOTOPIC COMPOSITION OF WATER WHICH HAS BEEN ENRICHED IN HEAVY ISOTOPES BY FRACTIONATION

by

H. A. E. MACKENZIE AND (MRS.) A. M. MILNER

OPSOMMING

Daar is gepoog om die noodsaaklikheid te vermy om die afsonderlike bydraers van HDO en $H_2{}^{18}O$ tot die oordigtheid van monsters water wat deur fraksionering met swaar isotope verryk is, eksperimenteel te bepaal. Die teorie lei tot die gevolgtrekking dat 'n fraksioneerkolom meer plate besit vir die skieding van $H_2{}^{16}O$ en $H_2{}^{18}O$ as vir die skeiding van H_2O en HDO. Deur 'n enkele parameter, die waarde waarvan mepiries bepaal is by die teorie van die verrykingsproses, in te sluit, is dit moontlik om die samestelling te bepaal van water, wat slegs deur middel van distillasie prosesse uit natuurlik water verkry is, mits die digtheid daarvan bekend is.

SUMMARY

An attempt has been made to obviate the need for determining experimentally the individual contributions of HDO and $H_2{}^{18}O$ to the excess density of water samples which have been enriched in heavy isotopes by fractionation. The theory leads to the conclusion that the platage of a fractionating column is greater for the separation of $H_2{}^{16}O$ and $H_2{}^{18}O$ than it is for the separation of H_2O and HDO. By introducing a single parameter, whose value is determined empirically, into the theory of the enrichment process, it is possible to calculate the composition of water which is derived from natural water by distillation processes only, provided that its density is known.

TABLE (100° C.)

Length of column (inches)	*Packing*	*Mode of distilling*	γd	γdo *Experimental*	*Calculated Eq.* 13	*r*	*Reference*
144	Stainless steel gauze rings	Total reflux at stillpot	150 125 100 98	84 66 62 61	85 70 58 57	1·31 1·18 1·38 1·38	3 3 3 3
240	Glass cylinders	Batch distn.	145	81	82	1·29	4
240	Brass helices	Two successive batch distns.	46 128	27 70	27 73	1·03 1·20	4 4
240	Stedman phospher bronze discs	Batch distn.	59 69	37 45	33 40	1·24 1·40	4 4
720	Brass helices	Batch distn.	49 74 122 184	34 44 78 111	28 43 70 104	1·52 1·18 1·54 1·56	4 4 4 4
144	Phosphor bronze gauze rings	Total reflux at stillpot	550	350	347	2·30	5

The excess density of a sample of water is a convenient measure of its degree of enrichment in deuterium and heavy oxygen. The separate contributions of the several isotopic species to the excess density have usually been found by "normalizing" the sample with respect to hydrogen or oxygen and re-determining the excess density. The procedure is laborious and we have sought to obviate it by developing a method whereby the isotopic composition can be computed. The calculation is to some extent empirical, but gives fairly good agreement with all the results available to us.

We shall denote the excess density (compared with natural water) in parts per million by the symbol γd and use the suffix D or O to indicate that a quantity refers to HDO or $H_2{}^{18}O$.

In order to develop the argument, the following assumptions will be made in the first instance:

(1) A sample of enriched water prepared by any series of distillation processes all a one temperature can be considered to have been brought into equilibrium at that temperature with normal water over an appropriate number of theoretical plates. It is emphasized that the sample must have been derived from natural water by distillation *only*; our calculation is not generally applicable, for example, to specimens prepared by mixing two separately enriched samples of water.

(2) The molecular volume of water in the liquid state is independent of its isotopic composition, i.e., the contribution of a heavy isotopic species of water to the density of a sample in which it occurs is in direct proportion to its molecular weight. This assumption, which has been generally adopted, gives rise only to negligible errors when dilute solutions of heavy water are concerned.

(3) In water which has a small deuterium content, all the deuterium is present in the form HDO, since a dynamic equilibrium between H_2O, HDO and D_2O is established by an ionic mechanism and, for dilute deuterium oxide solutions, the probability that HOD will occur is much larger than the probability that DOD will occur.

(4) The enrichment in heavy oxygen which occurs during distillation is all due to an increase in the $H_2{}^{18}O$ content of the water. It will be shown later that this seemingly drastic assumption does not, for small enrichments, lead to serious errors, because, not only is the difference between the vapour pressures of $H_2{}^{16}O$ and $H_2{}^{17}O$ only half that between the vapour pressures of $H_2{}^{16}O$ and $H_2{}^{18}O$, but, in addition, the $H_2{}^{17}O$ content of natural water is only one-fifth that of $H_2{}^{18}O$.

(5) The number of theoretical plates over which equilibrium between natural and enriched water is established is the same for the $H_2{}^{16}O/H_2{}^{18}O$ system as it is for the H_2O/HDO system.

If x is the weight fraction of an isotopic species present in an enriched sample, it can readily be shown that for $\gamma d << 10^6$, assumption (2) leads to the relationship:

$$10^5 x_O = 202 + \gamma d_O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Similarly, if all the deuterium were present as D_2O, we should have

$$10^5 x_{D_2O} = 20 + \gamma d_{D_2O},$$

but, in accordance with assumption (3), we prefer to write

$$10^5 x_D = 1{\cdot}9(20 + \gamma d_D) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The overall separation factors in the fractionation of water are given by:[1]

$$\alpha_D^{p_D+1} = \frac{x_D(1-X_D)}{X_D(1-x_D)} \quad \ldots\ldots(3)$$

and

$$\alpha_O^{p_O+1} = \frac{x_O(1-X_O)}{X_O(1-x_O)}, \quad \ldots\ldots(4)$$

where p_D and p_O are the platages with respect to the H_2O/HDO and $H_2{}^{16}O/H_2{}^{18}O$ separations, α_D is the ratio of the vapour pressures of H_2O and HDO, α_O is the ratio of the vapour pressures of $H_2{}^{16}O$ and $H_2{}^{18}O$ and X_D and X_O are the weight fractions of HDO and $H_2{}^{18}O$ in natural water. By assumption (5), $p_D = p_O$ and, therefore, from equations (3) and (4),

$$\log \alpha_O \cdot \log \frac{x_D(1-X_D)}{X_D(1-X_D)} = \log \alpha_D \cdot \log \frac{x_O(1-X_O)}{X_O(1-x_O)}. \quad \ldots\ldots(5)$$

Equations (1), (2) and (5) give:

$$\left\{\frac{0{\cdot}99962(1+0{\cdot}05\ \gamma dy)}{0{\cdot}99962-0{\cdot}000019\ \gamma dy}\right\}^{\log \alpha_O/\log \alpha_D} = \frac{0{\cdot}99798\ [1+0{\cdot}00495\ \gamma d\ (1-y)]}{0{\cdot}99798-0{\cdot}00001\ \gamma d\ (1-y)} \quad \ldots\ldots(6)$$

where $\gamma d_D = y \cdot \gamma d$ and $\gamma d_O = (1-y)\gamma d$, and, when γd is known, this may be solved for y by iteration. Provided γd is not too large, an approximate form of equation (6), viz.,

$$(1+0{\cdot}05\gamma dy)^{\log\alpha_O/\log\alpha_D} = 1+0{\cdot}00495\gamma d(1-y), \quad \ldots\ldots(7)$$

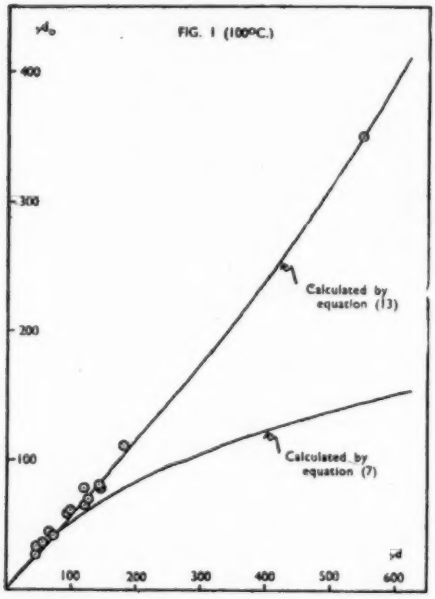
can be used for the calculation. In particular, for γd=600 and a distillation temperature of 100° C., the values of y calculated by equations (6) and (7) differ by less than one per cent.

The calculation of y has been carried through for distillations effected near 100° C., i.e., at atmospheric pressure, when[2] $\alpha_O = 1{\cdot}0046$ and $\alpha_D = 1{\cdot}0255$. The corresponding (calculated) values of γd_O are plotted against γd in Fig. 1, together with experimental points taken from the accompanying table. There is a sufficiently well-defined difference between the theory and experiment to demand a re-examination of the original assumptions.

Assumption (1) is essential to the development of the theory and will be kept. Assumptions (2) and (3) cannot give rise to the large discrepancy between experiment and the simple theory outlined above. The fourth assumption requires more detailed consideration. The effect of ignoring the enrichment in ^{17}O is not immediately obvious, but can be calculated to a good approximation. Consider, for example, a sample of water with $\gamma d = 100$. Equation (7) gives $y = 0{\cdot}489$ and therefore $\gamma d_D = 49$. From equation (3) the number of theoretical plates across which equilibrium has been established is 47 If we take the enrichment factor for $H_2{}^{17}O$ as 1·0023, then calculation shows that the weight fraction of $H_2{}^{17}O$ will be increased from its normal value of 40×10^{-5} to 45×10^{-5} by distillation across 47 theoretical plates. Thus, the weight fraction of $H_2{}^{18}O$ in the enriched sample is not $202 + \gamma d(1-y)$, but more nearly $197 + \gamma d(1-y)$, so that equation (7) becomes

$$(1+0{\cdot}05\gamma dy)^{\log\alpha_O/\log\alpha_D} = 0{\cdot}9752+0{\cdot}00495\gamma d(1-y),$$

which gives $y = 0{\cdot}460$ and $\gamma d_D = 46$. Iteration shows that a final value for $\gamma d_D = 46$ is obtained if the effect of ^{17}O enrichment is not ignored. The adoption of assumption (4)



therefore leads to over-estimation of the HDO content by 3 γd. Similarly, for $\gamma d = 600$, equation (7) gives $\gamma d_D = 428$ compared with the corrected value of $\gamma d_D = 416$. The adoption of assumption (4) cannot therefore be responsible for the disagreement between the simple theory and fact.

We are forced to conclude that assumption (5) is the cause of the discrepancy. Theoretically[1] the platage of a column is given by

$$p \sim \frac{(k_1 - k_{-1})Z}{L \cdot \log a}, \quad \ldots\ldots(8)$$

where k_1 and k_{-1} are the forward and reverse specific reaction rates for isotopic exchange between liquid and vapour, Z is the length of the column and L is the boil-up rate. There is evidently no reason why the platage should be the same for two different isotopic exchanges, even when the operating characteristics of the column are the same in the two cases. If we put

$$r = p_O/p_D, \quad \ldots\ldots(9)$$

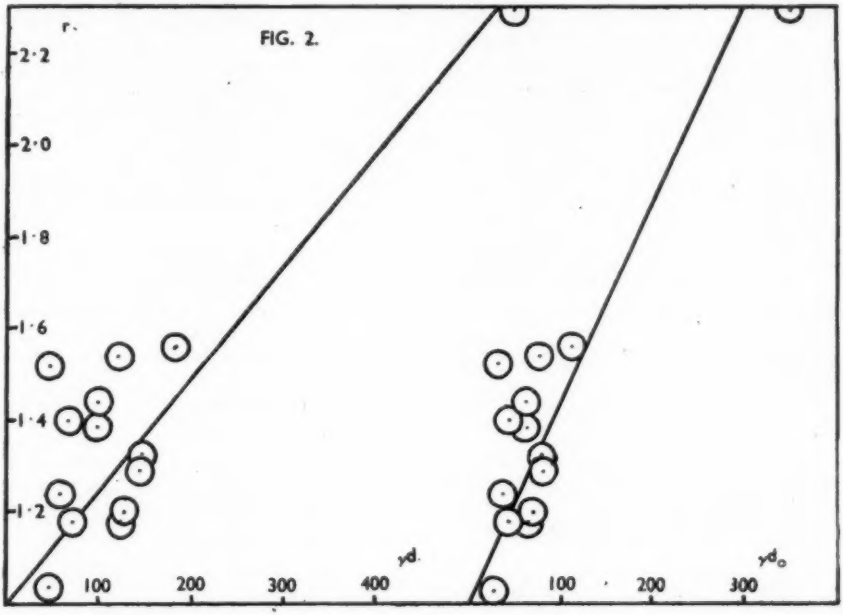
then, from equations (1), (2), (3), (4) and , (9)we obtain:

$$\frac{\log a_O/\log a_D}{(1 + 0{\cdot}05\gamma dy)} = \frac{1 + 0{\cdot}00495\gamma d(1-y)}{\exp.\left[(r - 1)\, p_D \log a_O\right]} \quad \ldots\ldots(10)$$

which replaces equation (7). Assuming that $p_D + 1 \sim p_D$, we have in addition, from equations (2) and (3):

$$p_D = \log(1 + 0{\cdot}05\gamma dy)/\log a_D. \quad \ldots\ldots(11)$$

Substitution of equation (11) in equation (12) gives:



$$(1 + 0{\cdot}05\gamma dy)^{\log\alpha_O/\log\alpha_D} = \frac{1 + 0{\cdot}00495\gamma d(1-y)}{\exp.\left\{(r-1)\log(1 + 0{\cdot}05\ \gamma d)^{\log\alpha_O/\log\alpha_D}\right\}}$$

which simplifies to:

$$(1 + 0{\cdot}05\gamma dy)^{r\log\alpha_O/\log\alpha_D} = 1 + 0{\cdot}00495\gamma d(1-y) \quad \ldots\ldots\ldots\ldots (13)$$

This can be solved for r for experimentally known values of γd and y. It is evident that equation (7) is the limiting form of equation (12) as $\gamma d \to 0$.

r has been evaluated at 100° C. from the experimental data given in the Table. Small variations in r cannot be considered significant, since, in most cases, the value of γd and consequently of y is known only to two significant figures. Nevertheless, r is best represented as a linear function of the total or the $H_2{}^{18}O$ enrichment, as Figure 2 shows. Using a value of r given by

$$r = 1{\cdot}00 + 2{\cdot}45 \times 10^{-3}\gamma d \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

y can be calculated from equation (13) for different values of γd. The calculated values of γd_O are given in the form of a curve in Fig. 1 and in the Table for comparison with the experimental values. The agreement is satisfactory.

We must emphasize, however, that the value of α_O is by no means established with certainty. The value used here is that of Riesenfeld and Chang[6] and was determined by distilling water and assuming that equilibrium was established across one theoretical plate. It is quite conceivable that more or less than one plate was achieved in practice.

The earlier work of Huffman and Urey[7] and Wahl and Urey[8] did, in fact, give a value of $\alpha_O = 1{\cdot}003$ at 100° C., which is considerably lower than that of Riesenfeld and Chang. If α_O is taken as 1·003, larger values of r are obtained. On the other hand, Dostrovsky, Hughes and Llewellyn[9] have suggested that the available estimates of α_O are too small. If this is indeed the case, then, for total enrichments of up to about 1,000 γd, r must differ less from unity than our calculations would suggest.

It seems established, however, that r is greater than unity. This may be explained tentatively in the following way: Isotopic exchange during the distillation of water takes place according to the reactions:

$$H_2{}^{16}O\ (l) + HD^{16}O\ (g) = HD^{16}O\ (l) + H_2{}^{16}O\ (g)$$
$$\text{and } H_2{}^{16}O\ (l) + H_2{}^{18}O\ (g) = H_2{}^{18}O\ (l) + H_2{}^{16}O\ (g)$$

Presumably the mechanism is a simple exchange of molecules between the gaseous and liquid phases, facilitated by the large wetted surface which the column packing provides. We suggest that the oxygen exchange can proceed by another mechanism as well, which we formulate thus:

$$H_2{}^{16}O\ (l) + X{-}{}^{18}O\ (s) = H_2{}^{18}O\ (l) + X{-}{}^{16}O\ (s)$$
$$H_2{}^{18}O\ (g) + X{-}{}^{16}O\ (s) = H_2{}^{16}O\ (g) + X{-}O\ (s),$$

where X—O represents a solid compound of oxygen available in the column either as an oxide coating on the metal of the packing or in the form of glass. If these reactions do occur, the specific reaction rate for exchange and hence the platage will be larger in the case of $H_2{}^{16}O/H_2{}^{18}O$ than in the case of H_2O/HDO.

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STUDIES ON ISOTOPES

PART II. THE APPROACH TO ISOTOPIC EQUILIBRIUM DURING FRACTIONAL DISTILLATION WITH APPRECIABLE HOLD-UP IN THE STILLPOT

by

H. A. E. MACKENZIE AND P. N. MALHERBE

OPSOMMING

Daar word angetoon dat 'n wysiging van Urey se teorie, oor die benadering tot isotopiese ewewig gedurende fraksionele distillasie, wat gebruik kan word in die gevalle waar 'n aansienlike ophoping in die distilleerkol plaasvind, 'n voldoende en ook nuttige weergawe van die feite gee.

SUMMARY

A modification of Urey's theory[1] of the approach to isotopic equilibrium during fractional distillation, which can be employed in cases where there is appreciable hold-up in the stillpot, is shewn to yield an adequate and useful representation of the facts.

THEORETICAL CONSIDERATIONS

The discussion will concern the separation of two isotopically different species of a liquid by fractional distillation through an insulated column at thermal equilibrium. We shall denote the two species "light" and "heavy" and indicate them by suffices 1 and 2 respectively.

In a distillation, the simple process fractionation factor, α, is given by the ratio of the vapour pressures of the two liquids which are to be separated[2], and, from the definition[3] of α, we have, therefore:

$$\alpha = p_1/p_2 = \frac{n_2'\,(1-N_2')}{N_2'\,(1-n_2')}, \qquad \ldots\ldots(1)$$

where p_1, p_2 are the vapour pressures, n_2' is the mole fraction of the heavy constituent in the liquid phase and N_2' is the mole fraction in the vapour phase when liquid and vapour are in equilibrium. The overall separation factor, A, depends on α and the platage, p, of the column, thus:[3]

$$A = \alpha^{p+1} = \frac{n_2\ (1-N_2)}{N_2\ (1-n_2)}, \qquad \ldots\ldots(2)$$

where n_2 and N_2 are now the mole fractions at the bottom and top of the column respectively.

It is convenient and legitimate to replace the mole fractions in (1) and (2) by the corresponding weight fractions, whereupon

$$\alpha = p_1/p_2 = \frac{x_2'\,(1-X_2')}{X_2'\,(1-x_2')}, \qquad \ldots\ldots(3)$$

and

$$A = \alpha^{p+1} = \frac{x_2\ (1-X_2)}{X_2\ (1-x_2)}, \qquad \ldots\ldots(4)$$

where x_2, X_2, x_2' and X_2' are weight fractions of heavy constituent.

At a particular point in the column, the rate of transport of heavy constituent down the column is given by [1]

$$T = lx_2' - LX_2', \quad \ldots\ldots(5)$$

where L is the flow of vapour up the column and l is the flow of liquid down the column, both expressed as weights per unit time. For a column under total reflux,

$$l = L \quad \ldots\ldots(6)$$

and so

$$T = L(x_2' - X_2'). \quad \ldots\ldots(7)$$

When operation of a column is begun, equilibrium is at first established across just one theoretical plate at the total reflux end of the column, so that the initial transport in any distillation can be obtained by substituting the value of x_2' from (3) into equation (7). The initial rate of transport is thus:

$$T_i = \frac{LX_2'(\alpha-1)(1-X_2')}{1+(\alpha-1)X_2'}. \quad \ldots\ldots(8)$$

If $X_2' << 1$, $\alpha \sim 1$, this may be written

$$T_i = LX_2'(\alpha-1). \quad \ldots\ldots(9)$$

Urey[1] has assumed that the isotopic exchange between liquid and vapour takes place in accordance with an equation of the type:

$$M_1\,(l) + M_2\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M_2\,(l) + M_1\,(g),$$

where k_1 and k_{-1} are the forward and reverse specific reaction rates respectively and M_1, M_2 are the light and heavy molecular species. If one neglects diffusion along the length of the column, the distillation obeys the differential equations:

$$\left.\begin{aligned} h(\partial x_2'/\partial t) - l(\partial x_2'/\partial z) - k_1x_2'(1-X_2') + k_{-1}X_2'(1-x_2') &= 0 \\ H(\partial X_2'/\partial t) + L(\partial X_2'/\partial z) + k_1x_2'(1-X_2) - k_{-1}X_2'(1-x_2') &= 0 \end{aligned}\right\} \ldots\ldots(10)$$

where h and H are the weights of vapour and liquid hold-up per unit length and where the weight fractions are those obtaining at a distance z from the bottom of the column. For steady operation at total reflux, equation (6) is applicable, and in addition

$$(\partial X_2'/\partial t) = (\partial x_2'/\partial t) = 0 \quad \ldots\ldots(11)$$

and

$$X_2' \sim x_2', \quad \ldots\ldots(12)$$

so that the equations (10) become simply

$$L(\partial X_2'/\partial z) + (k_2 - k_{-1})X_2'(1 - X_2') = 0. \quad \ldots\ldots(13)$$

Integration yields

$$\int_{X_2}^{x_2} \frac{dX_2'}{X_2'(1-X_2')} = \int_z^0 \frac{(k_1 - k_{-1})dz}{L}, \quad \ldots\ldots(14)$$

$$\text{or } \log \frac{x_2(1-X_2)}{X_2(1-x_2)} = (k_1 - k_{-1})\cdot\frac{z}{L}, \quad \ldots\ldots(15)$$

where z is now the total length of the column.

Comparison of equations (4) and (15) gives:

$$p + 1 = (k_1 - k_{-1})\cdot z/L\cdot\log\alpha. \quad \ldots\ldots(16)$$

Since the platage of a column at a given temperature is known to depend on the nature of the packing material as well as on z and L, the occurrence of equation (16) implies that the k_1 and k_{-1} used in the theory are rates which include the effect of the packing material on isotopic exchange. This has an important bearing elsewhere.[6]

Huffman and Urey[3] have developed an elegant and simple physical treatment of the approach to equilibrium in a column. Unfortunately the formulation of this treatment has led them to adopt certain mutually contradictory assumptions and to make unnecess-

ary approximations. In addition they have not dealt with the commonly encountered practical situation where distillation is effected using appreciable hold-up in the still-pot rather than a flash boiler. Since the only other satisfactory treatment of the approach to equilibrium, that of Bartky and Dempster,[4] deals merely with cases where isotopic enrichment is extremely small, we have thought it worth while to develop the theory of Huffman and Urey further.

They have represented the approach to equilibrium as an increase with time in that length of the column which is in the steady state, while the non-equilibrium region becomes shorter. The rate at which the steady-state zone grows upwards form the still-pot will depend on the rate at which the heavy constituent is transported down the column. Bearing in mind the appropriate boundary conditions, we have

$$\int_0^z x_2' \cdot \mathrm{Hdl} - \int_0^z X_2 \cdot \mathrm{Hdl} = \int_0^t \mathrm{Tdt}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (17)$$

where X_2 is the weight fraction of heavy constituent in the starting material and x_2' is the weight fraction at the upper end of the steady-state zone when it is growing by a length dl in a time dt. t is the time taken for the length z of the column to reach the steady state. It is, of course, assumed here that total reflux occurs at the stillpot.

We propose to elaborate somewhat on these ideas. We regard the approach to equilibrium as an increase with time in the number of theoretical plates which have come into play above the stillpot, i.e., those plates in the steady state zone. The platage of the steady state zone will increase during operation of the column from zero to its maximum, equilibrium value, the latter being the platage of the whole column. Alternatively since only those plates in the steady state zone are in use at any time, the effective H.E.T.P. for the whole column will decrease with time from infinity to its minimum, equilibrium, value.

This interpretation does not seem to have been used by previous workers, including Huffman and Urey (*loc. cit.*). Instead, they have simplified and used equation (17) in the following way:

(i) The assume that T is constant, which is clearly in disagreement with fact since T must decrease from its initial value, T_1, to zero when the steady state is reached over the whole column.

(ii) They then replace T by the value of T_i given by equation (9). Equation (17) then takes the form:

$$\int_0^z \frac{B \cdot \alpha^{kz}}{1 + B \cdot \alpha^{kz}} \cdot \mathrm{Hdl} - \int_0^z X_2 \cdot \mathrm{Hdl} = LX_2(\alpha - 1) \cdot t, \quad \ldots\ldots\ldots\ldots\ldots (20)$$

where k is the number of theoretical plates per unit length of the column and $B = X_2/(1-X_2)$. The result, when the integrals are evaluated, is

$$X_2 \log(X_2/x_2) + (1-X_2)\log\{(1-X_2)/(1-x_2)\} = \frac{LX_2(\alpha-1)p\log\alpha}{H'} t, \quad \ldots\ldots\ldots (21)$$

where p is the total number of plates in the column and H′ is the total liquid hold-up of the column.

In order to obtain p, Huffman and Urey plot the experimental values of the left hand side of (21) against time, measure the slope of the resulting straight line and equate this to the coefficient of t. We consider, however, that p is to be regarded essentially as a variable dependent on x_2, whose value changes during the approach to equilibrium. The fact that a straight line plot is obtained in the case of the distillation of water can be due only to a compensating effect in the errors attentdant on the sasumptions which are made. More specifically, p and T are assumed to be constant, whereas the theory requires that they should increase and decrease respectively during the approach to equilibrium. A useful result may, in certain cases, be obtained if the increase in p is so offset by the decrease in T that the product p.T remains constant, but there seems to be no reason why this should be true in general.

The following alternative treatment of equation (17) is therefore proposed.

It is recognized, to start with, that the rate of increase in the weight fraction of heavy isotopic species in the stillpot, dx_2/dt, is itself a function of time, say $\phi(t)$. Now the actual weight of heavy constituent in the stillpot, W, is given by

$$W = x_2 \cdot W^\circ, \quad \ldots\ldots(22)$$

where W° is the total weight of water in the stillpot. Hence, $dW/dt = (dx_2/dt)\cdot W^\circ = \phi(t)\cdot W^\circ$, $\ldots\ldots(23)$

and this is, by definition, the rate of transport of heavy constituent into the stillpot. Equation (17), therefore, can be written

$$\int_0^z x_2' \cdot H dl - \int_0^z X_2 \cdot H dl = \int_0^{t'} W^\circ \cdot \phi(t) \cdot dt, \quad \ldots\ldots(24)$$

giving

$$X_2 \log(X_2/x_2) + (1-X_2)\log\{(1-X_2)/(1-x_2)\} = \frac{W^\circ (x_2 - X_2)\log a}{H'} \cdot p \cdot \quad \ldots\ldots(25)$$

p, the number of plates in the steady-state zone of the column after time t, can now be evaluated from the experimentally measured value of x_2 and the known values of X_2, a, W° and H'. The effective H.E.T.P. of the column after time t is given by $h = z/p$, where z is the total length of the column. The approach to isotopic equilibrium can then be demonstrated graphically as shown below.

TABLE I

97·5° C.; $H_2O/HDO = 1{\cdot}0255^7$; $H_2{}^{16}O/H_2{}^{18}O = 1{\cdot}0046^7$; z = 144 ins.

yd	^xHDO	$^xH_2{}^{18}O$	$xHDO$	$xH_2{}^{18}O$	*p*		*h (ins.)*	
					(1)	(2)	(1)	(2)
187	·00192	·00308	·00038	·00202	64	93	2·3	1·5

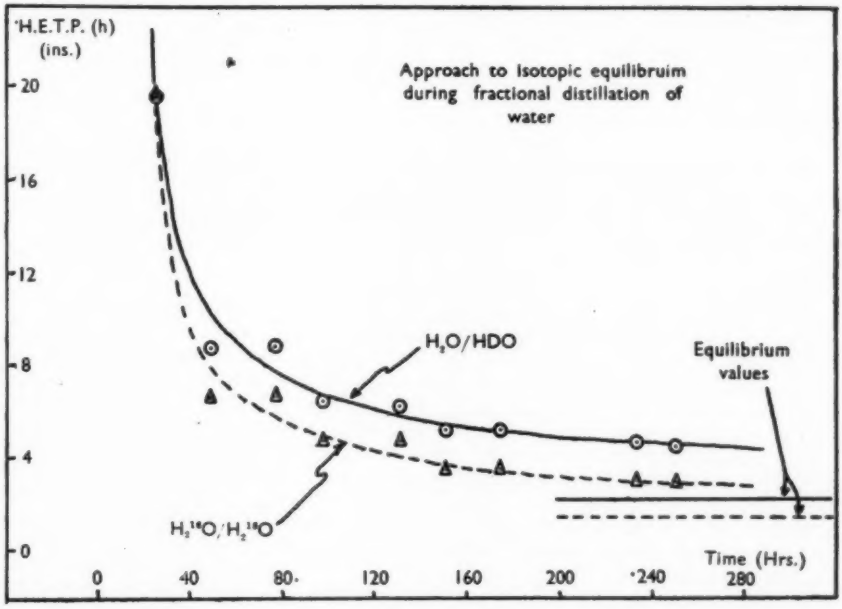
(1) refers to the H_2O/HDO system and (2) to the $H_2O/H_2{}^{18}O$ system.

TABLE II

$97 \cdot 5°C$; z.W°/H′ = 90 ins.; $\theta = X_2 \log(X_2/x_2) + (1-X_2)\log\left((1-X_2)/(1-x_2)\right)$

t(hrs.)	γd.	$10^5 \cdot x_{HDO}$	$10^5 \cdot x_{H_2{}^{18}O}$	$10^5\,\theta$		$10^5\,(x_2 - X_2)$		h (ins.)	
				(1)	(2)	(1)	(2)	(1)	(2)
0	0	38	202	—	—	—	—		
25	14	48	211	0·50	0·08	10	9	19·6	19·7
49·5	44	72	228	3·80	0·69	34	26	8·8	6·6
76·5	43	72	227	3·80	0·65	34	25	8·8	6·7
98·0	65	89	240	7·68	1·39	51	38	6·5	4·8
131·5	67	91	240	8·19	1·39	53	38	6·3	4·8
151·5	91	110	255	13·3	2·60	72	53	5·3	3·6
174·5	90	110	254	13·3	2·51	72	52	5·3	3·6
234·0	111	127	266	18·3	3·66	89	64	4·8	3·1
250·5	117	133	269	20·2	3·97	95	67	4·6	3·0

(1) refers to the H_2O/HDO system and (2) to the $H_2O/H^{18}O$ system.



Application of the theory to the fractional distillation of water.

The results of experiments 6 and 7 in a study by the authors on the rectification of water using stainless steel gauze rings as packing[5] will serve to illustrate the application of the theory. The weight fractions of HDO and $H_2{}^{18}O$ have been calculated from the measured excess densities by a method outlined elsewhere.[6]

The data of experiment 6 and the application of equation (4) give the equilibrium values of the H.E.T.P. for the column used by the authors. The values are given in Table I.

Equation (25) has been used to calculate, from the data of experiment 7, the H.E.T.P. of the column at different times during the approach to equilibrium. The results are given in Table II and shown graphically in the Figure.

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STUDIES ON ISOTOPES

PART III. THE PERFORMANCE OF STAINLESS STEEL GAUZE RING PACKING IN THE ISOTOPIC FRACTIONATION OF WATER

by

H. A. E. MACKENZIE AND P. N. MALHERBE

OPSOMMING

'n Laboratorium-stookketel vir die rektifisering van water word beskryf. Die stookketel is uit goedkoop en algemeen verkrygbare materiaal vewaardig en sluit bykomstighede in wat 'n noukeurige beheer oor toevoer en drukverlies uitoefen, en waardeur vars water in die ketel ingelaat kan word om die isotopies—ligte distillaat te vervang. Die twaalf-voet rektifiserende deel van die ketel is met $\frac{1}{16}$ duim, 100-maas roesvrye staal—gaasringe gevul.

Die resultate van verskeie distillasies toon aan dat hierdie pakking gebruik kan word om goeie verrykings van $H_2{}^{18}O$ en HDO te verkry, mits die toevoer stadig is. Die kenmerkende eienskappe van die pakking is in besonderheid bestudeer en die kolom is tweemaal tot isotopiese ewewig gebring. Die verrykings van swaar isotope wat in die twee gevalle verkry is, is gelykstaande aan toename in digtheid van 180 en 187 dele per miljoen.

Daar is bevind dat herhaalde gebruik die maksimum toevoer verminder en die doeltreffendheid van die pakking verhoog, vermoedelik as gevolg van die reinigingswerking van die stoom op die roesvrye staal oppervlak.

Die werkverrigting van die staalringe is aansienlik swakker as wat angegee word vir identiese fosfor bronsringe soos deur Dostrovsky en Hughes gebruik. Die enigste waarskynlike verklaring skyn te wees dat die metale verskillende oppervlakeienskappe het.

Des nieteenstaande is 'n H.E.T.P. van so min as 1·5 duim in die geval van suurstof-isotope behaal.

SUMMARY

A laboratory still for the rectification of water is described. The still is constructed from cheap and readily available materials and embodies accessories which give close control of throughput and pressure drop and by means of which fresh water can be fed into the column to replace the isotopically light distillate. A 12-ft. rectifying section is packed with $\frac{1}{16}$ in., 100 mesh stainless steel gause rings.

The results of several distillations show that this packing may be used to achieve useful enrichments of $H_2{}^{18}O$ and HDO, provided that low throughputs are employed. The characteristics of the packing have been studied in detail and the column has twice been run to isotopic equilibrium. The enrichments of heavy isotopes achieved in the two cases are equivalent to increases in density of 180 and 187 parts per million.

The limiting boil-up rate has been found to decrease and the efficiency of the packing to increase with usage, presumably due to a cleansing action of the steam on the stainless steel surface.

The performance of the stainless steel rings is markedly inferior to that claimed for the otherwise identical phosphor bronze rings used by Dostrovsky and Hughes.[1] The only likely explanation seems to be that the metals have different surface characteristics. Despite this, an H.E.T.P. of as little as 1·5 in. in the case of the oxygen isotopes has been achieved here.

INTRODUCTION

The efficiency claimed by Dostrovsky and Hughes[1] for the $\frac{1}{16}$in. phosphor bronze gauze rings which they used as a packing material in the rectification of water is greater than that of any other packing material which has been reported in the literature. From the authors' estimate that their 12-ft. column had 450 theoretical plates it would appear that they achieved an H.E.T.P. of as little as 0·32 in. The packing also allows a very high throughput per unit cross section; with a $\frac{3}{4}$-in. diameter column, Dostrovsky and Hughes operated at a throughput of 500 ml. of water per hour. Even better performance, in the case of organic liquids, is claimed by the makers for similar stainless steel rings (an H.E.T.P. of 0·2 in. for a 1-in. diameter column with a boil-up rate of 500 g./hr. of a normal heptane-methylcyclohexane mixture) but they aver that the rings are unsuitable for the distillation of liquids, such as water, which have a high surface tension, because the rings tend to "lock" with liquid. It is of interest that this should take place with stainless steel rings but not, apparently, with those of phosphor bronze, and one object of this work has been to test out the former packing under carefully controlled conditions.

Description of the still

(*a*) *Stillpot*. The stillpot, which was a cylinder of 650 ml. capacity, was constructed of 18-gauge stainless steel sheet and is represented diagramamtically in Fig. 1 (*a*). The stillpot was heavily lagged as shown with a mixture of asbestos and binding materials which caused the lagging to dry out to a porous adherent coating after it had been applied wet.

(*b*) *Rectifying section*. The packed section of the column consisted of a 13-ft. long tube of glass with an internal diameter of 2 cm. The greater part of the tube was surrounded by a vacuum jacket consisting of a 12-ft. long, 3-in. internal diameter iron pipe, fitted with reducing sockets at each end bringing the diameter down to 2 in. The 2 cm. glass tube was held in position by a pair of greased rubber stoppers fitting both the glass tube and the reducing sockets snugly. The reducing sockets were screwed on, then brazed and the brazing was finally covered with solder to ensure vacuum tightness. The jacket was pumped out hard twice a day through a $\frac{3}{8}$-in. diameter brass tube brazed on to its side. Inside the jacket were three brightly polished cylindrical copper reflectors, of diameters about 1·5, 2 and 2·5 in., coaxial with the glass and iron tubes. They were kept in position by a few small cork spacers, staggered in such a way as to minimize conduction.

The column was mounted vertically above the stillpot and attached thereto by a short length of thick-walled rubber tubing, inside which the stillpot lead and the end of the column touched. The rubber tube was then bound with two layers of insulation tape. This type of connexion was found experimentally to be quite reliable in operation and preferable to the metal-to-glass cone and socket which was a first employed, but which proved too frangible for convenience.

Before the column was joined to the stillpot, a tangle of piano wire, threaded with gauze rings, was forced into its lower end. This proved to be an effective support for the packing and made it possible to avoid the use of separate liquid and vapour paths between the stillpot and the packing. The latter are usually necessary with other types of packing support because even a slight constriction at the base of a small diameter column can induce sporadic flooding and unsteadiness of operation.

(*c*) *Stillhead and reflux device*. (Fig. 3). The total condensate from the column was fed into one end of a 14-litre reservoir, initially filled with "normal" water, and an equal volume of reflux, pre-heated to the correct temperature, was forced back into the column from the other end. The figure shows how the design of the reservoir minimized the mixing of condensate and feed water. In this way stripping of heavy isotopes from the feed water at the top of the column was avoided. The fourteen glass tubes of which the reservoir consisted were each about 1 metre long and of l-litre capacity and successive tubes were joined with long pieces of small diameter glass tubing.

During normal operation, when cocks E, H only are open, steam travels up the unpacked section of the column, through the pre-heater jacket, where it is partially condensed, and finally to the total condenser. All the condensate collects in the vertical tube, J, from where it runs through cock H to the top of the reservoir. An equal volume of water is then displaced from the reservoir through cock E and, after being heated to the temperature of steam in the pre-heater, it runs into the column through the lagged tube, K. J reaches lower than K so that a failure of the power supply to the stillpot heater does not lead to siphoning of all the water in the reservoir into the column.

The reservoir water is replaced with "normal" (distilled) water every time a total of about 14 litres of condensate has passed into it. This is done as follows: Cock G is opened very slowly so that there is no sudden change in the water level in J. H, E are

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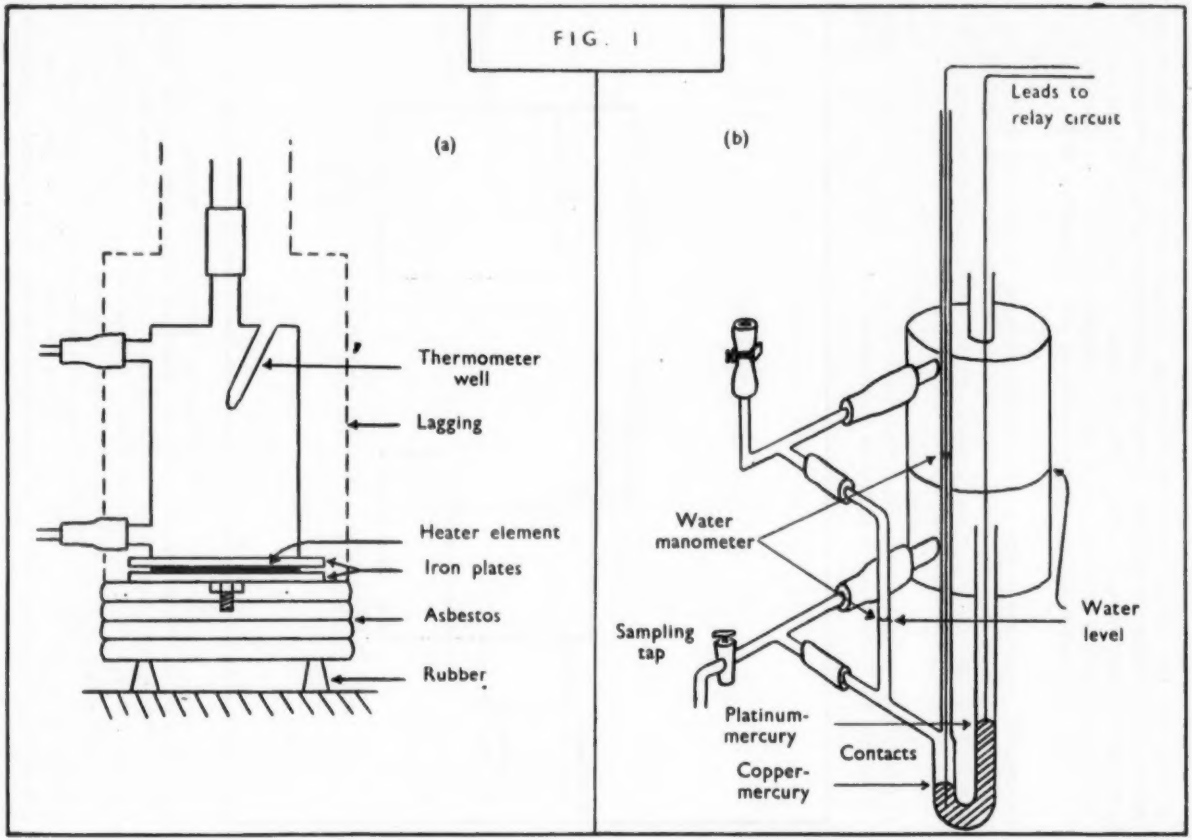
FIG. 1



closed and F opened, so that the auxiliary reservoir, L, is now alone in use. C is opened, whereupon a little air rushes into the reservoir, showing that this part of the system is under reduced pressure during operation. The reservoir is now emptied through B. B is then closed and A opened so that fresh water from the supply tank, M, fills the reservoir. A is then closed when the water reaches C and C is closed after A. At C the reservoir is now under atmospheric pressure, which is greater than its normal working pressure, and care must be taken when opening H to avoid a sudden change in the water level in J. E is then opened, F, G closed and normal operation resumed.

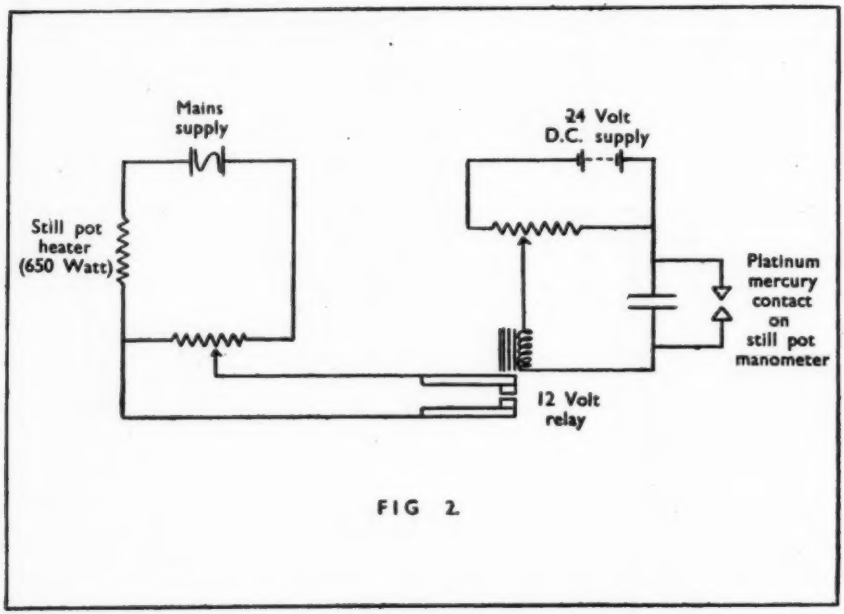


FIG 2.

Small column throughputs are measured by closing H and measuring the rate of rise of water in the arm J which is suitably graduated. Large throughputs are determined by closing H and collecting condensate at N for a short time.

Before the stillhead was attached to the column, the latter was packed by filling it with water and then pouring in the stainless steel rings. A tangle of piano wire, threaded with rings, was introduced into the column above the packing to prevent displacement of the latter during pre-flooding. Such displacement was found to occur if no precautions were taken.

(*d*) *Pressure-drop measurement and throughput control.* The pressure-drop across the packed section of a column is a measure of the flow of material through the column, so that its constancy is generally supposed to imply a constant throughput. The pressure drop is often measured by a manometer which has one limb connected to the vapour in the stillpot and the other joined to the condenser. Some workers have put traps on either side of the manometer in order to catch stray vapour.[2] Following the example of

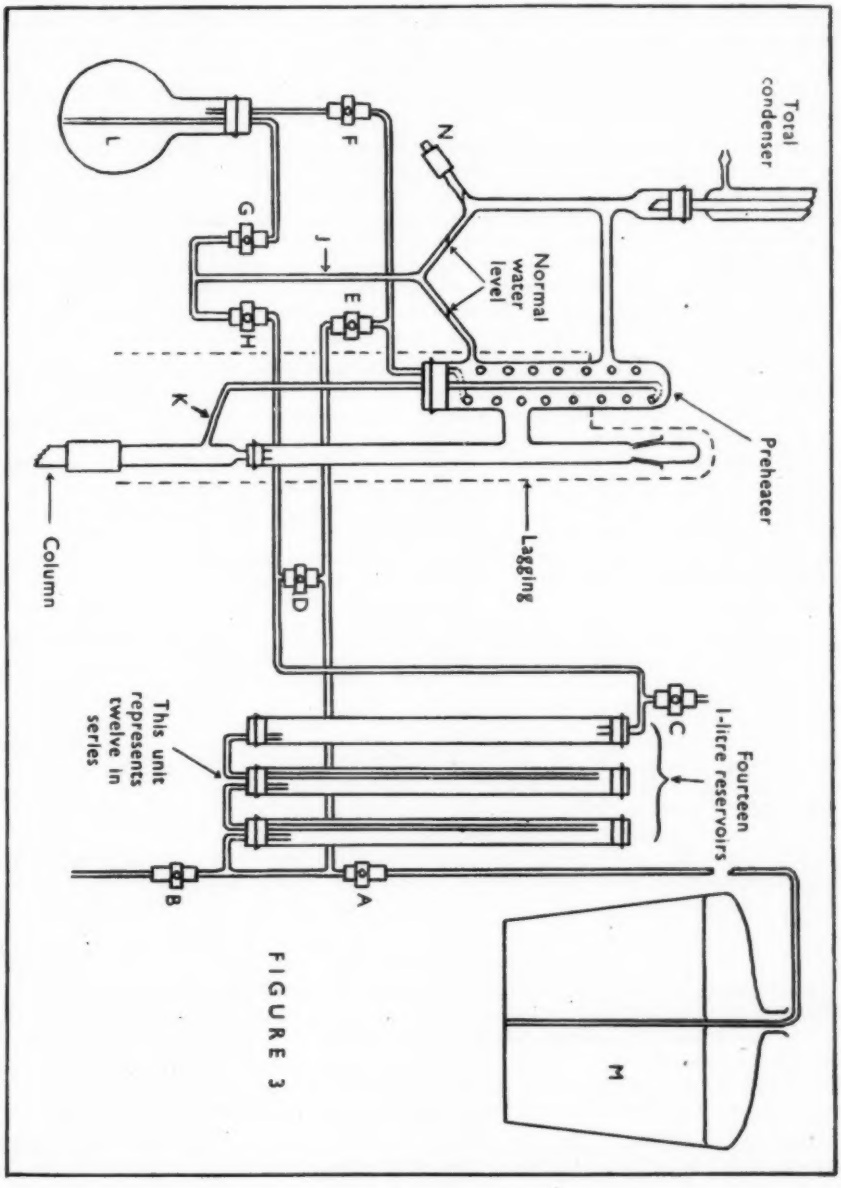

Total condenser
N
L
F
G
J
Normal water level
E
H
K
Preheater
Column
Lagging
D
C
Fourteen 1-litre reservoirs
This unit represents twelve in series
B
A
M

FIGURE 3

Willingham and Rossini[3] an attempt was made here to use mercury and butyl phthalate manometers in parallel, the former arranged to operate a relay controlling the heat input and the latter to record the pressure drop. A 1-litre flask was placed in series with the manometers to serve as a baffle which would smooth out short term pressure fluctuations and also to act as a vapour trap.

When the column was put into operation, vapour was found to diffuse along the lead from the stillpot to the manometer. This lead became hot and vapour condensed along its whole length and into the baffle flask. Simultaneously the column throughput fell practically to zero. A deliberate increase in heat input resulted immediately in an increase in throughput, but gradually the latter would fall off again to an impracticably low value, while the rate of condensation in the manometer system increased. The problem was at first quite baffling and does not seem to have been reported previously. Lagging the manometer system, changing the diameter of the leads either way and the introduction of traps did nothing more than alter the rate at which the column throughout fell off.

The problem evidently has not been encountered with non-aqeous systems because the vapours most frequently dealt with in rectification have much larger densities and lower rates of diffusion than water vapour. Even if diffusion were halted by fitting a total condenser to the manometer lead, the above method of pressure-drop measurement would give spurious results because the condenser and manometer would constitute a dynamic system making its own unknown contribution to the pressure-drop. That this is indeed the case was evident from the fact that a recorded pressure-drop of 20 cm. butyl phthalate corresponded to a stillpot temperature 3·0° C. above that at atmospheric pressure, implying a true pressure-drop of about 100 cm. butyl phthalate. In addition, the method would be wasteful of heat and would not make for steadiness of column operation.

The difficulty was finally resolved by using manometers connected directly to the water in the stillpot as shown in Fig. 1 (*b*). Diffusion was thus prevented and the true pressure-drop could readily be obtained. The temperature of the boiling water in the stillpot was then found to correlate with the recorded pressure-drop.

The mercury manometer in Fig. 1(*b*) was used to operate a relay which controlled the input of heat into the stillpot in the manner indicated in Fig. 2. The circuit was designed to cater for the rather large fluctuations in the local mains supply voltage, which was shown by a recording voltmeter to vary from 180 to 230 volts during a 24-hr. period. The system was quite successful and the pressure-drop could be kept constant to within about 1 per cent. over a period of weeks, provided that no flooding occurred. The limiting throughput itself gradually fell over a long period (a feature of the packing which will be referred to again later), but short-term operation was perfectly steady.

Column operation and characteristics

(*a*) *Preflooding.* Packings made from wire gauze must hold a film of reflux in order to function effectively, so that a thorough wetting is important. Nickels[4] was the first to report that a flooding treatment leads to an increase in fractionation efficiency. Pre-flooding may be effected either by pouring the liquid through the column[5] (a method now obsolete) or by increasing the boil-up rate until the liquid is driven right up to the condenser.[6, 3] Distillation is then begun after a period of distillation at total reflux.

The makers of Dixon gauze rings have patented a novel method of pre-flooding[6] which gives less variable efficiencies than the technique of increasing the boil-up rate

above its limiting value. The method is to overfill the stillpot so that the whole packed section is submerged. The liquid is then boiled with a heat input equivalent to that which will be used in the subsequent distillation. When the liquid is boiling steadily it is gradually run out of the stillpot till a convenient level is obtained and distillation is begun after a period of total reflux. Even this method was not very suitable for the present work as transmission of heat up the column was very slow. The procedure adopted, therefore, was to introduce water slowly into the stillpot, while heat was supplied at a convenient rate, so that all the time the stillpot was being filled and the packing being submerged, the boiling did not cease. When the boiling water reached the stillhead the heat input was adjusted to the desired value and, after about thirty minutes of steady boiling, water was slowly tapped out of the stillpot and allowed to drain from the column.

(*b*) *Volume of column and packing material.* The volume of water required to fill the packed section of the column was 1,400 ml. and, of this, 75 ml. was displaced by the addition of 600 g. of packing. Thus, in the packed section of the column the packing itself occupied 75 ml. and the voids 1,325 ml.

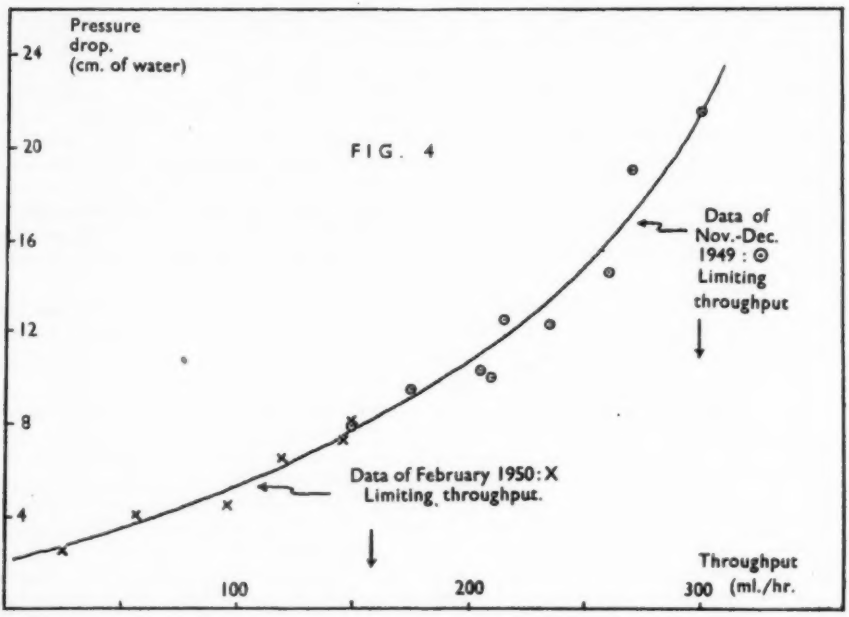
(*c*) *Hold-up.* After the column was first packed, the water was allowed to drain out until the column seemed empty and then for a further two hours. The volume of water retained in the column was 56 ml. After several months of operation, the column was was allowed to drain for six days. A sample of packing was then removed from the lower end and the loss of weight incurred by drying this sample at 130° C. gave the static hold-up as 50 ml. of water, in good agreement with the earlier estimate. The dynamic hold-up was considerably larger than this; it was estimated in one run to be about 170 ml. with an experimental uncertainty of about 50 ml. This quantity could not be measured very accurately as changes in ambient temperature brought about variations in the weight of water held in the 14-litre stillhead reservoir and consequently in the stillpot itself.

(*d*) *Heat loss from the still.* Measurement of the heat input by means of simultaneous voltage and current observations on the heater element, together with the measurement of throughput, gave the total heat loss from the still as about 130 watts, of which, it was estimated, only a small fraction came from the packed section of the column. The column itself, therefore, could be regarded as very nearly adiabatic.

(*e*) *Correlation between pressure-drop and throughput.* Fig. 4 shows two plots of pressure-drop against throughput. The one set of observations was made during November and December, 1949 and the other during February, 1950 after the column had been in almost continuous operation for over three months. The limiting boil-up rate, i.e., the maximum throughput which does not give rise to flooding, seems to be a function of the total time of past operation and falls off with usage of the packing. It must be presumed that the steam has a slow cleansing action on the packing, leading to a gradual increase in the degree of wetting and in the dynamic hold-up and consequently to a fall in the limiting boil-up rate. In support of this suggesttion it may be noted that repacking of the column in April, 1950 resulted in a temporary increase in the limiting boil-up rate. In addition, a more rapid approach to isotopic equilibrium, implying a greater separation efficiency, correlated with the lower limiting boil-up rate.

Sampling and measurement of isotopic enrichment

Samples were withdrawn from the stillpot, when necessary, through the tap attached to the manometer system (Fig. 1 (*b*).) In order that the presence of "dead" liquid in the lower side limb and in the manometers might not vitiate the results, a little air was



gently blown in at the tap in order to agitate the water immediately before sampling. The tap was then opened very slightly and water was run out drop by drop into a 10 ml. sampling flask. The size of the samples varied from four to six ml. After sampling, the water in the tube outside the tap was always pushed back into the pot by gentle blowing.

Isotopic enrichment was assessed by determining the excess density of a sample, after careful purification, relative to local tap water which had been subjected to the same purification process. The method of purification adopted was that of Briscoe.[7] Excess densities were determined by the falling drop method,[8] using a bromobenzene-xylene mixture as the dropping liquid, constancy of temperature to within 0·001° C. and a micropipette for drop delivery which was essentially the same as that of Keston, Rittenberg and Schoenheimer[8]. Five dropping times each were determined for "normal" water, the sample and a standard sample of enriched water known to have an excess density of 377 parts per million, in this order. If the mean dropping times were respectively t_0, t and t_1, then the excess density of the sample, γd, in parts per million, was calculated from the formula:

$$\gamma d = 10^6 (d - d_0) = \frac{377(1/t - 1/t_0)}{(1/t_1 - 1/t_0)}$$

RESULTS

The results obtained in some of the distillation runs are given in the accompanying Table.

DISCUSSION

Despite the statement by the makers that their stainless steel gauze ring packing with rings $\frac{3}{16}$ x $\frac{1}{16}$ in. cannot be used for the rectification of liquids with a high surface tension, this research has shown that auseful enrichment in the heavy isotopes of oxygen and hydrogen is readily obtained by distilling water. In all, about 2 litres of water having a mean enrichment equivalent to an excess density of more than 100 parts per million has been collected.

However, it seems impossible to distil at the rate of 500 ml. per hour when stainless steel rings are used although Dostrovsky and Hughes (loc. cit.) have employed such a throughput in a similar column packed with phosphor bronze rings. The limiting boil-up rate was found to be about 300 ml. per hour with the stainless steel rings and it decreased appreciably with usage.

The highest (equilibrium) enrichment obtained was equivalent to an excess density of 187 parts per million. This implies[9,10] a platage for the column of 93 theoretical plates for the separation of the oxygen isotopes, with a corresponding H.E.T.P. of 1·5 in.

When these figures are compared with the 450 plates obtained by Dostrovsky and Hughes, it would seem that there is a very real difference between the separation efficiencies

TABLE

Expt. No.	*Total hrs. run*	*Throughput (ml./hr.)*	*Excess density of stillpot water — parts per million*	*Vol. of water in stillpot (ml.)*	*Remarks*
1	139	210 (mean)	123	370	Throughput varied to study effect on pressure drop.
4	180	220 (mean)	138	214	Flooding occurred twice due to relay failure. Relay circuit then changed to one described in this paper. Dynamic hold-up — 170 ml.
6	476	20	135	200	Perfectly steady. Absence of one author due to illness debarred use of higher throughput.
	476	Increased to 120			
	517		164		
	566		180		
	623		176		
	630		180	180	Isotopic equilibrium Leak developed. 100 ml. fresh water added through condenser.
	687		145	280	
	735		178		
	764		187	250	Isotopic equilibrium.
7	25	160	14	300	
	49·5		44	300	
	76·5		43	300	Heater fused. 23 hr. stagnant period, not included in total hrs. run.
	98·0		65	300	
	131·5	180	67	300	Failure of local water supply led to losses through the condenser.
	151·5		91		
	174·5		90		
	234·0	210	111		
	250·5		117	150	

of stainless steel and phosphor bronze ring packings. The advantage of the lower throughput and the fresh water reflux used here are apparently more than offset by inherent properties of stainless steel which adversely affect its efficiency as a packing material for use in the rectification of water. The only likely explanation seems to be that there is a difference in surface characteristics.

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STUDIES IN ISOTOPES

PART IV. CATALYSIS OF ISOTOPIC EXCHANGE BETWEEN GASEOUS OXYGEN AND LIQUID WATER

by

H. A. E. MACKENZIE AND (MRS.) A. M. MILNER

OPSOMMING

Daar is gepoog om die isotopiese uitruiling tussen suurstof en water onder laboratorium toestande te kataliseer. Geen noemenswaardige wisseling vind plaas in die teenwoordigheid van metaaloksiede of hidroksiede of organiese stowwe wat in oksidasie-reduksie reaksies kan deelneem nie-. Daar is egter vas gestel dat uitruiling wel in die teenwoordigheid van H_2O_2 of ander stowwe wat die opbreking van H_2O_2 kataliseer, plaasvind.

Aangesien katalase juis so 'n stof is en aangesien hierdie ensiem in alle groen plante voorkom kan die feit dat die suurstof wat gedurende fotosintese vrygestel word die selfde isotopiese samestelling het as die water waarin die plant gedoop is nie langer aanvaar word as 'n bewys dat die meganisme van fotosintese die vervaardiging van suurstof alleenlik uit die water behels nie.

SUMMARY

Attempts have been made to catalyse the isotopic exchange between oxygen and liquid water under laboratory conditions. No appreciable exchange occurs in the presence of metallic oxides or hydroxides, or of organic substances capable of entering into oxidation-reduction reactions. It is established, however, that exchange does take place in the presence of H_2O_2 and of substances which catalyse the decomposition of H_2O_2.

Since catalase, in particular, is one such substance and since this enzyme exists in all green plants, the fact that the oxygen produced during photosynthesis has the same isotopic composition as the water in which the plant is bathed can no longer be accepted as proof that the mechanism of photosynthesis involves the production of oxygen solely from the water.

For abour fifteen years a phenomenon known as the "Dole effect", namely, the existence of a higher proportion of ^{18}O in atmospheric oxygen than in natural water, has been a well-established experimental fact.[1] The discrepancy arises if, as is generally assumed,[2] the oxygen of the atmosphere is derived mainly from the photosynthesis of green plants and the phenomenon has given rise to much speculation and conjecture.

In an attempt to find a possible explanation of the Dole effect on the basis of isotopic exchange between oxygen and water based on some mechanism other than photosynthesis, we have sought for a catalyst which would accelerate the exchange reaction to a measurable speed at normal temperatures and under atmospheric pressure.

The water used throughout these experiments had been isotopically enriched by fractional distillation. The total excess density was 150 parts per million of which 84 was due to heavy oxygen and 66 due to deuterium.

To obtain intimate contact between the heavy water containing a potential catalyst and an atmosphere of oxygen, 2½-litre cylindrical bottles were dried and then filled with tank oxygen at room temperatures and pressure. 6 cc. samples of heavy water were introduced together with the catalyst and the bottles were tightly stoppered. They were then rolled slowly and continuously on electrically-operated rollers for periods varying from seven to fourteen days. The water was thus spread in a thin, moving film on the bottle walls and presented a large and changing surface to the oxygen.

After the period of rolling the water was poured out of the bottle and its density was determined after purification. The generally accepted method of purification was used, viz.,

(1) Samples of about 3 cc. were heated with about 0·02 g. of Na_2O_2 and a slight excess of $KMnO_4$; then distilled completely *in vacuo*.

(2) The distillate was warmed with about 50 mg. of P_2O_5 and then distilled *in vacuo* directly into the float chamber for density determination.

As it was found that mere heating with alkaline permanganate did not give reproducible results a novel technique was introduced. The sample of water with the sodium peroxide and permanganate was placed in a round-bottomed flask of about 10 cc. capacity connected by a ground-glass joint with a long glass reflux tube. The sample was boiled gently over a micro-flame for about an hour. This had the effect of removing volatile impurities as well as oxidizing organic matter, but did not cause any loss of water. Using this technique, density determinations could be reproduced to within one part per million. In all cases the density was confirmed after repurification.

The micro-flotation method of Briscoe[3] was used for density determinations. Pietermaritzburg tap water was used as a standard for comparison.

The method demands accurate temperature control. It is necessary that the thermostat should maintain any desired temperature to within 0·001° C. for a period of several minutes. At the same time the thermostat must be so controlled that its temperature can be raised or lowered rapidly by increments of 0·01° C. To achieve this a toluene regulator with a finely threaded screw in the side arm for re-adjustment was used. No wire proved sufficiently rigid for the make-and-break so a steel needle was used. The relay was an electronic one of the type devised by Leisegang, Mackenzie and Malherbe[4], the heating element being a 60-watt electric light bulb, whose output could be varied readily by means of a variable series resistance. This arrangement gave a simple on-off regulator which could maintain the temperature steady only to within 0·003°, but, if the thermoregulator was continuously shaken by means of a slack wire attached to the stirrer motor, a "flicker" control resulted, which maintained a constant temperature for long periods. With this "flicker" control contact was made and broken about 500 times a minute when a steady temperature had been reached, but if the temperature dropped slightly the flickering became slower, the light remaining on for slightly longer periods than it was off, so that there was a greater heat input the further the temperature was below that desired. The thermostat was used in the temperature range 30–32° C.

The substances which were to be tried as catalysts were prepared as follows:

Manganese dioxide: From A.R. reagents by the Guyard reaction.

$$6{\cdot}5 \text{ mg. } MnSO_4, 4H_2O + 3{\cdot}6 \text{ mg. } KMnO_4.$$

Copper hydroxide: From A. R. reagents.

$$5 \text{ mg. } NaOH + 12{\cdot}6 \text{ mg. } CuSO_4, 5H_2O.$$

In both these cases the reagents were added to the heavy water already in the bottle with oxygen so that the desired compounds were freshly formed *in situ*.

Ferroin: 2 drops used from stock.
Tannic acid: 2 mg. from stock.
Pyrogallol: 2 mg. from stock.
Quinhydrone: 2 mg. from stock.
Hydrogen peroxide: 3 drops of 90 volume H_2O_2.
Platinized asbestos: About 0·5 cc. of the commercially available material

Palladized asbestos: About 0·5 cc. of the material freshly made by the method of Zelinsky and Borishoff.[5]

Colloidal platinum: Made by striking an arc between fine platinum wires held under the heavy water to be treated.

Catalase: Prepared from beef liver by the method of Sumner and Dounce.[6]

All substances tested as catalysts were used in such small quantity that any isotope exchange between the catalyst and the heavy water would result in only a negligible depletion of the water in heavy oxygen. Where liquids were used due attention was paid to the slight dilution of the heavy water.

The first results obtained are given in the upper section of the accompanying table. They show that no exchange took place between oxygen and liquid water alone, nor was such an exchange catalysed by the inorganic oxide or hydroxide, nor by the organic substances capable of enetering into oxidation-reduction reactions. However, there does appear to have been significant exchange in the presence of hydrogen peroxide and of platinized or palladized asbestos. The colloidal platinum, therefore, which might have been expected to act as well, had not been protected and the lack of catalysis was presumably due to the rapid coagulation which occurred.

Since the indications were that a peroxide mechanism might be involved, a further five experiments were carried out as follows:

(1) 6 cc. of heavy water were rolled for eight days with one drop of 90 volume hydrogen peroxide and 2·25 litres of oxygen.

(2) 7 cc. of heavy water were rolled for eight days with 2·5 litres of oxygen and with about 20 mg. of catalase, largely in suspension. The catalase activity was tested before and after rolling by measuring the volume of oxygen that was released by 1 cc. of this suspension from 2 cc. of 10 volume hydrogen peroxide. 9·95 cc. of oxygen was obtained before rolling and 8·61 cc. after.

(3) 6 cc. of heavy water with about 20 mg. of catalase in suspension and 1 drop of 10 volume hydrogen peroxide were rolled for eight days with 2·5 litres of oxygen. During this experiment the catalase activity declined almost to zero, the volumes of oxygen collected in the test being 9·95 cc. before rolling and 0·7 cc. after.

(4) 6 cc. of heavy water were rolled for eight days with about 0·5 cc. of palladized asbestos and 2·5 litres of oxygen.

(5) 6 cc. of heavy water, already partly exchanged, with an excess density of 137·4 parts per million of which 71·6 was due to heavy oxygen, were rolled for a further six days with palladized asbestos and 2·5 litres of oxygen.

In all cases exchange occurred and the results are given in the lower section of the table

An attempt to improve on the method for mixing the oxygen and water was unsuccessful and merely serves to indicate the efficiency of the "bottle-rolling" technique. 5 cc. of heavy water (100 parts per million, of which 62 was due to oxygen) was placed together with palladized asbestos in a bubbler with a sintered glass bottom. Through this a stream of dry oxygen, 50 litres in all, was passed. The time occupied was about 50 hours. Any water vapour passing over was collected in a trap and returned periodically to the bubbler. Although the oxygen passed through the water as a stream of very fine bubbles there was a loss of only 3·5 parts per million in density. No loss in density was observed in a control experiment where the palladized asbestos was omitted.

DISCUSSION

It seems to be established with certainty that the isotopic exchange reaction between oxygen and liquid water can be induced to proceed at a measurably rapid rate by the introduction either of hydrogen peroxide or of a substance which has the power to catalyse the decomposition of hydrogen peroxide. It is well recognized that catalase and finely divided platinum or palladium are such substances.

For the reaction,

$$H_2O_2\,(l) = H_2O\,(l) + \tfrac{1}{2}O_2,$$

$\triangle G^\circ_{298} = -28{\cdot}7$ k. cal. (from tables) implying an equilibrium constant of about 10^{21}. It may be considered that a catalyst for the decomposition of H_2O_2 simply brings about this equilibrium rapidly, the position of equilibrium favouring almost completely the formation of water and oxygen, the concentration of peroxide being about 10^{-21} mole. litre^{-1} with oxygen at atmospheric pressure.

It would seem, then, that equilibrium between water and oxygen might be established through the intervention of hydrogen peroxide, which will be present always in a very minute quantity when water and oxygen are brought together in the presence of peroxide decomposing catalysts. Even under the influence of catalysts the rate of exchange between water and oxygen, under the conditions used by us, is small. The limiting rate process might well be the dissolution of oxygen in the water or the diffusion of oxygen in the neighbourhood of the oxygen-water interface. On the other hand, the experimental finding that the rate of exchange was roughly the same with four catalysts may indicate that the reaction between oxygen and water involves at least two processes:

$$(1)\ H_2O + \tfrac{1}{2}O_2 = H_2O_2$$
$$(2)\ H_2O_2 + H_2O^* = H_2OO^* + H_2O.$$

If (1) is extremely slow, this will be the rate-determining process in the absence of catalysts and the exchange between water and oxygen will also be extremely slow. If (2) is a faster reaction and the introduction of a catalyst speeds up reaction (1), without affecting (2), then the exchange between oxygen and water in the presence of a catalyst will proceed at a rate determined by (2), the rate being independent of the catalyst or its concentration.

The fact that isotopic exchange occurs between oxygen and water in the presence of catalase is of considerable importance. The tracer experiments of Ruben, Randall, Kamen and Hyde,[7] in which it was found that oxygen evolved during photosynthesis by Chlorella has the same isotopic composition as the water in which the plants are bathed and bears no relation to that of the CO_2 available, have been generally recognized as critical evidence that photosynthetic oxygen is derived from water and not from carbon dioxide. The interpretation of their experiments is now open to question. The fact that water and oxygen are brought into contact in plant cells, which contain catalase, would cause exchange to take place, so that photosynthetic oxygen, whether derived from water or carbon dioxide, may be expected to show the same isotopic composition as the water available to the plant, *merely* because it has been present with the water in the plant cell. In addition, there is likely to be more intimate contact between the oxygen and water in the plant than there has been in our experiments, so that the catalase-accelerated exchange between oxygen and water may be far more rapid than we have found it to be *in vitro*.

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TABLE

Substance added	*Time of rolling days*	*Flotation temp. of sample minus that of tap water (° C.)*		*Excess density in p.p.m.*				*Percentage exchange*
				Total		*Due to ^{18}D*		
		Initial	*Final*	*Initial*	*Final*	*Initial*	*Final*	
None	7	0·499	0·498	149·7	149·4	84·0	83·7	—
Manganese dioxide ...	7	0·499	0·498	149·7	149·4	84·0	83·7	—
Copper hydroxide ...	7	0·499	0·495	149·7	148·5	84·0	82·8	—
Ferroin	7	0·499	0·498	149·7	149·4	84·0	83·7	—
None	9	0·499	0·501	149·7	150·3	84·0	84·6	—
Palladium-asbestos ...	9	0·499	0·474	149·7	142·2	84·0	76·5	—
Platinum-asbestos ...	9	0·499	0·482	149·7	144·6	84·0	78·9	—
Colloidal platinum ...	9	0·499	0·506	149·7	151·8	84·0	86·1	—
90 vol. hydrogen peroxide	7	0·499	0·460	149·7	138·0	84·0	72·3	—
Quinhydrone	7	0·499	0·496	149·7	148·8	84·0	83·1	—
Pyrogallol	7	0·499	0·494	149·7	148·2	84·0	82·5	—
Tannic acid	7	0·499	0·506	149·7	151·8	84·0	86·1	—
Palladium-asbestos ...	8	0·499	0·452	149·7	135·6	84·0	69·9	47
Hydrogen peroxide ...	8	0·499	0·454	149·7	136·2	84·0	70·5	47
Catalase	8	0·499	0·458	149·7	137·4	84·0	71·7	44
Catalase + H_2O_2 ...	8	0·499	0·458	149·7	137·4	84·0	71·7	40
Palladium-asbestos ...	6	0·458	0·426	137·4	127·8	71·6	62·0	35

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THE CATALYSED DEHYDRATION OF OXALIC ACID IN ACETIC-ACID ACETIC ANHYDRIDE MIXTURES

by

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OPSOMMING

Die katalitiese werking van swawelsuur en oorchloorsuur, en van piridien op die dehidratering van oksaalsuur met asynsuuranhidried is bestudeer, deur die spoed van gasontwikkeling uit oplossings in asynsuur-asynsuuranhidried mengsels te meet.

Daar is vasgestel hoe afhanklik die reaksiesnelheid van die konsentrasies van swawelsuur en oorchloorsuur by 30° C. is. Die byvoeging van 'n baie klein hoeveelheid van enige van die sure, veroorsaak aansienlike toename in snelheid. Verdere vermeerderings in die suurkonsentrasies veroorsaak geen ooreenkomstige vermeerderings in die snelheid nie. Die energie en entropie van aktivering is vir verskeie reaksiemengsels bereken.

Die reaksie verloop anders wanneer kataliese met piridien teweggebring word. Die reaksie snelheid is in daardie geval eweredig aan die piridien konsentrasie.

'n Meganisme wat in ooreenstemming met die eksperimentele befindings is word voorgestel terwyl die snelheid van die ongekataliseerde reaksie bepaal word deur die eenvoudige bimolekulêre proses van oksaalsuur met asynsuur anhidried molekule, skyn die gekataliseerde reaksie plaas te vind met die vinnige vorming van 'n gemengde anhidried van oksaalsuur en asynsuur.

SUMMARY

The catalytic effect of sulphuric and perchloric acids and of pyridine on the dehydration of oxalic acid by acetic anhydride has been studied by measuring the rate of gas evolution from solutions in acetic acid-acetic anhydride mixtures.

The dependence of the reaction rate at 30° C. on the concentrations of the sulphuric acid and perchloric acid has been determined. Addition of either acid in very small amount brings about a marked increase in the rate; a further increase in acid concentration, however, does not lead to a proportionately ncreased rate. The activation energy and entropy of activation have been calculated for different reaction mixtures.

The reaction follows a different course when catalysis is effected by means of pyridine, the rate of reaction being proportional to the pyridine concentration.

A mechanism has been proposed which is in accord with the experimental findings. While the rate of the uncatalysed reaction is determined by a simple bimolecular process involving oxalic acid and acetic anhydride molecules, the catalysed reaction seems to proceed via the rapid formation of a mixed anhydride of oxalic and acetic acids.

INTRODUCTION

England and Mackenzie[1] have found that the uncatalysed dehydration of oxalic acid by acetic anhydride in media which consist of acetic acid and acetic anydride is simply a bimolecular reaction. The transition state theory applied to such a simple mechanism gives a complete explanation of the experimental facts. Catalysis by mineral acids and by potassium acetate were reported, but, in the latter case, precipitation of potassium oxalate accurs which debars a kinetic investigation of this catalysis. The authors suggest that a study of the catalysed reactions might provide an insight into acid-base equilibria of the type $AcOH_2^+ + Ac_2O = Ac^+ + (AcOH)_2$, and thus into the properties of the acetyl ion, Ac^+. One object of the present work has been to put this suggestion into effect.

Mackenzie[2], in the light of an indicator study of acetic acid-acetic anhydride mixtures, suggests that sulphuric acid may ionize, in the presence of acetic anhydride, according to the equation: $(HO)_2SO_2 + Ac_2O = (HO)_2SO_2Ac^+ + OAc^+$. In contrast, the ionization of perchloric acid is acidic[3]:

$$HClO_4 + Ac_2O = Ac^+ + ClO_4^- + AcOH.$$

A second object of this research has been to find support for or evidence against this supposed difference between sulphuric and perchloric acids, by comparing their effects as catalysts.

In both objects the research, in a sense, has been unfruitful, since a satisfactory explanation of the facts has emerged without the need for considering the precise character of the acid-base equilibria involved.

No kinetic study of the catalysed reaction between oxalic acid and acetic anhydride has previously been reported, although Schierz[4] has investigated the base-catalysed reaction between formic acid and acetic anhydride and Whitford[5] has used pyridine to accelerate the dehydration of oxalic by acetic anhydride. The latter author has noted the formation of a pyridine acid oxalate during the reaction.

PREPARATION OF MATERIALS

Oxalic acid, acetic acid and acetic anhydride were purified by the methods of England and Mackenzie.[1] Analysis of the oxalic acid gave 100·1 per cent $(COOH)_2$. Water-free stock solutions of sulphuric and perchloric acids in acetic acid were prepared by mixing the concentrated mineral acid (of "Analar" quality) with acetic acid and just enough acetic anhydride to react stoichiometrically with all the water. The mixture was then made up to any desired volume in a measuring flask with acetic acid. Pyridine was distilled and allowed to stand over potassium hydroxide to remove water. Stock solutions of pyridine were prepared by dissolving a weighed amount of pyridine in acetic acid in a volumetric flask.

DETERMINATION OF REACTION RATES

The progress of a reaction was followed by means of the apparatus described earlier.[1] The amount of oxalic acid decomposed at any time was calculated from the measured volume of gas evolved by the method worked out by England and Mackenzie[6], [1], due correction being made for the solubility of carbon dioxide in the reaction mixture and for the vapour pressure of the latter. Two different acetic acid-acetic anhydride mixtures were used, the one containing 20 per cent and the other 80 per cent v/v acetic anhydride. As a general rule, each reaction was followed until roughly one third of the oxalic acid had been decomposed.

In order to record the progress of the reaction in any particular run, values for $(a - x/2)$ have been computed; a being the initial concentration of oxalic acid in moles per 20 ml. of reaction mixture and the x the number of moles of CO and CO_2 produced. Since 20 ml. of reaction mixture was invariably used for a run, $(a - x/2)$ is also the number of moles of undecomposed oxalate surviving in solution.

EXPERIMENTAL RESULTS

(*a*) Catalysis by sulphuric acid

The plot of log $(a - x/2)$ against time gives a well-defined straight line, indicating the first order character of the reaction in the presence of sulphuric acid and a large excess of acetic anhydride. It has been assumed, therefore, that the formation of sulphoacetic acid[7] is relatively so slow that it does not complicate the kinetics of the reaction. The experimental first order constants, j, defined by the equation

$$-\frac{dc_{(COOH)_2}}{dt} = j \cdot c_{(COOH)_2},$$

for two different solvent mixtures and several sulphuric acid concentrations at 30° C. are given in Table I. Next to each first order constant is given in parenthesis the number of the corresponding experiment.

A marked positive catalytic effect is shown, the first order constant being roughly three times that for the uncatalysed reaction. A plot of the first order constant, j, against

the concentration of sulphuric acid is shown in Fig. 1. Some rates were measured for reaction mixtures with a very high content of sulphuric acid. However, it was found that the first order constant increased only very slightly when the concentration of sulphuric acid was changed from 0·002 M. to 0·7 M.

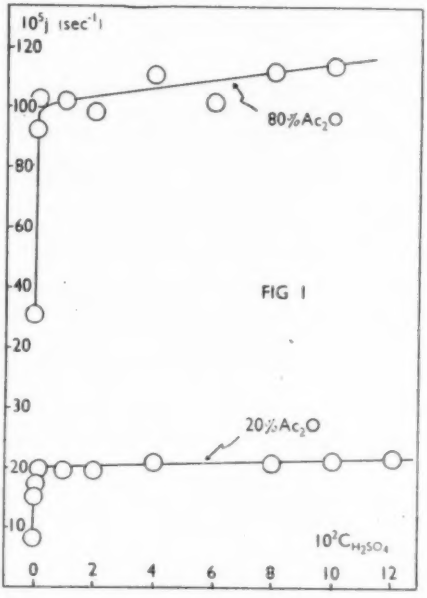


FIG 1

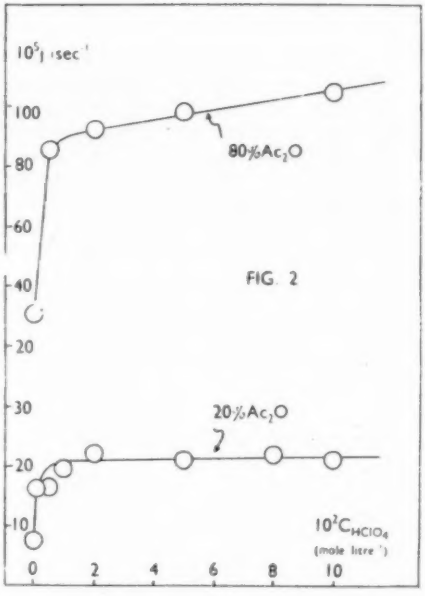


FIG. 2

Arrhenius energies of activation have been obtained from rate constants applying over a temperature range from 22° to 35° C. with 0·10 and 0·05 M. sulphuric acid solutions. Values of j and the activation energies, E, derived therefrom are given in Table II. Energies of activation and the corresponding entropy increments of activation are given in the summarizing Table V. The entropy of activation has been computed by assuming direct proportionality between j and the concentration of acetic anhydride; i.e., it has been assumed that j is related to the specific reaction rate, v, by the equation

$$j = v\left({}^{c}Ac_2O + v'\right)$$

The validity of this assumption is demonstrated by the selection of results collected in Table VI. The fact that it is necessary to include a constant, v′, suggests some medium effect which is, however, small, and has therefore, not been studied explicitly. A frequency factor, A, has first been calculated from the equation $v = A \cdot e^{-E/RT}$, and hence the entropy of activation, $\triangle S^*$, from the relationship $A = e \cdot (kT/h) \cdot \exp(\triangle S^*/R.)$ These calculations involve the implicit assumption that the rate determining process is a reaction between a species whose concentration is proportional to the concentration of oxalic acid and a species whose concentration is proportional to the concentration of acetic anhydride. This assumption, however, is consistent with the facts.

(*b*) Catalysis by perchloric acid

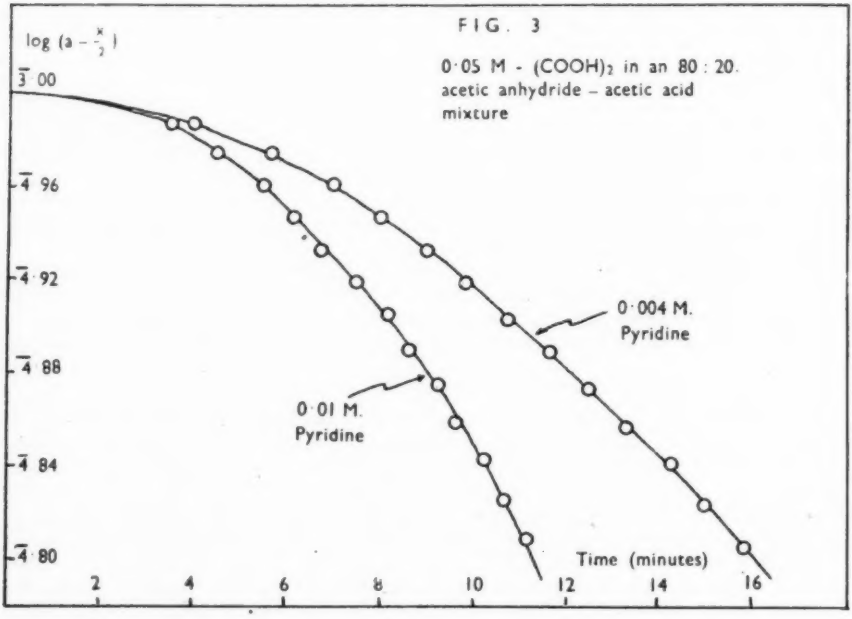
The effect of perchloric acid on the reaction rate simulates very closely that of sulphuric acid. The first order character of the reaction is preserved. The experimental results and the calculated energies and entropies of activation are summarized in Tables III, IV and V and Fig. 2.

(*c*) Catalysis by pyridine

During the course of a pyridine-catalysed reaction, the reaction rate decreases less with time than it would if the disappearance of oxalic acid obeyed a first order law. The effect becomes more marked with increasing pyridine concentration. The deviation from first order is demonstrated in Fig. 3, where a pair of typical plots of log (a—x/2) against time are given. Determinations of the solubility of carbon dioxide in acetic acid-acetic anhydride mixtures showed that the distribution ratio was not significantly altered by the addition of pyridine in concentrations about the same as those used in the kinetic work. Thus the deviation from first order is a kinetic effect and not simply a solubility effect.

In order to have the reaction proceed at a conveninetly measurable rate concentrations of pyridine had to be used which were much smaller than those employed in the case of the two mineral acids. Runs were observed, at 30° C., with varying pyridine concentrations in a reaction mixture containing 80 per cent by volume of acetic anhydride and 0·05 M. oxalic acid.

FIG. 3



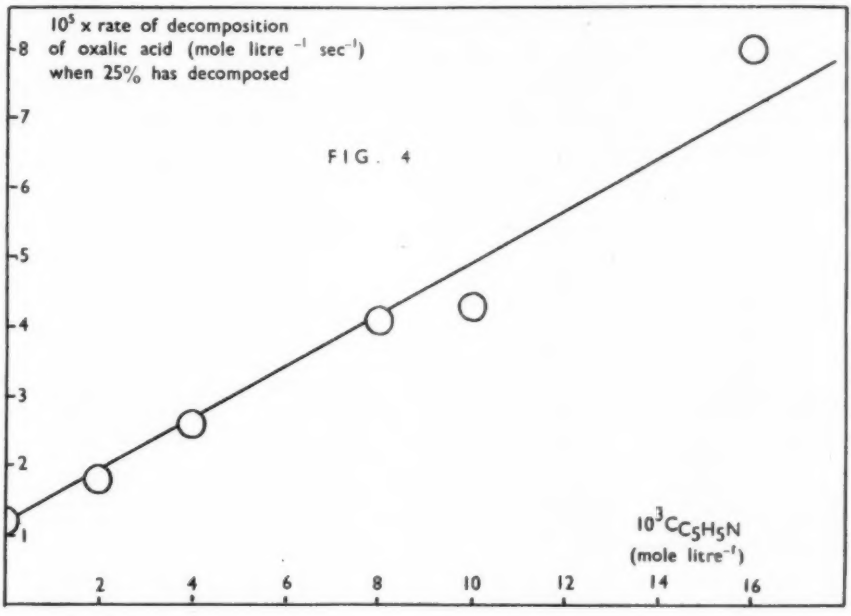


FIG. 4

As it was not possible to determine the specific reaction rate from a straight line plot of log $(a - x/2)$ against time, we have drawn tangents to the curves obtained by plotting $(a - x/2)$ against time, at points representing the decomposition of one-quarter of the oxalic acid. The reaction rates obtained in this way are summarized in Table VII and plotted against the concentration of pyridine in Fig. 4. It appears that the rate of reaction increases steadily with the concentration of pyridine and is, very roughly, proportional to it. More detailed experimental investigation of the pyridine-catalysed reaction must necessarily await a better understanding of the reaction which may make it possible to determine the rate of reaction more accurately than has been done above.

DISCUSSION

Their interpretation of the uncatalysed reaction has led England and Mackenzie (*loc. cit.*) to speculate on the nature of the mineral acid and acetate ion catalysed reactions and they have suggested that the mechanism in these cases might involve the acetyl ion, Ac^+, which would exist in appreciable concentrations when a mineral acid is present. Thus the reaction rate might be increased by an increase in the mineral acid concentration

The facts now available, however, point unambiguously at the mechanism of the catalysed reaction. The salient features are:

(1) The rate of reaction is not consistently increased by an increase in acid concentration. Therefore, there cannot be a single rate-determining process which involves a molecule of the mineral acid or any ionic species derived from it by protolytic reactions in solution.

(2) The psuedo first order character of the decomposition persists even when the reaction is catalysed. The rate-determining process, therefore, must still involve oxalic acid or some species derived therefrom.

The only mechanism which appears to cater for these conclusions and is at the same time consistent with the kinetics of the uncatalysed reaction is the following:

(i) $(COOH)_2 + Ac_2O = AcO{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}OH + AcOH$

(ii) $AcO{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}OH + Ac_2O = \text{Products.}$

If it is assumed that reaction (i) is rate determining in the absence of mineral acid, i.e., reaction (ii) is rapid compared with (i), then the kinetics of the uncatalysed reaction will be essentially the kinetics of reaction (i). If now the introduction of mineral acid facilitates reaction (i) but has no effect on reaction (ii), then the latter will become rate-determining and its kinetics will be observed in any experimental study. In neither case does the rate-determining process involve mineral acid or species derived therefrom and in both cases (providing a reasonable excess of acetic anhydride is available), the reaction will be pseudo first order with respect to oxalic acid.

Despite the attractive simplicity of this mechanism, it will not bear close scrutiny for it gives no explanation of the significant variations in the energy and entropy of activation which are summarized in Table V. It must be modified to meet the requirements:

(1) In 20 per cent v/v acetic anhydride medium, catalysis by minimal quantities ofa cid leaves the energy of activation unchanged but increases the entropy of activation to a numerically smaller value.

(2) In this same medium, further increases in mineral acid concentration lead to a lowering of the activation energy while the entropy of activation becomes more negative.

(3) In 80 per cent v/v acetic anhydride medium the energy of activation is consistently lower for the catalysed reaction than it is for the uncatalysed reaction, whereas the entropy of activation is about the same.

These facts demand the introduction of at least one more reaction into the mechanism in order to explain the difference between reactions in media containing respectively 80 and 20 per cent of acetic anhydride.

The effect of mineral acid on energy and entropy of activation in 20 per cent acetic anhydride medium may be associated with the small but significant effect of acid concentration on the reaction rate where the former is greater than 0·01 M.; an explanation of this is possible only if the mechanism is elaborated still further. It has proved necessary, in fact, to introduce reactions involving acetylium (the acetyl ion) and the acetate ion.

In view of the basic character of pyridine it can certainly be expected to ionize in acetic acid-acetic anhydride medium to give pyridinium and acetate ions.

We shall set out now a mechanism for the dehydration of oxalic acid, based on the preceding considerations, which seems to explain the facts relevant both to the acid-catalysed and the uncatalysed reactions; it is, at the same time, the simplest mechanism which meets all the requirements.

Proposed mechanism for the dehydration of oxalic acid

(i) $(COOH)_2 + Ac_2O \xrightarrow{k_1} AcO{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OH + CH_3COOH.$

(ii) $AcO{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{C}}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{C}}{-}OH \xrightarrow{k_2} AcOH + CO_2 + CO.$

(iii) $AcO{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{C}}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{C}}{-}OH + Ac_2O \xrightarrow{k_3} AcOH + Ac_2O + CO_2 + CO.$

(vi) $AcO^- + AcO{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{C}}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{C}}{-}OH \xrightarrow{k_4} AcOH + AcO^- + CO_2 + CO.$

(v) $Ac^+ + AcO{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OH \xrightarrow{k_5} AcOH + Ac^+ + CO_2 + CO.$

In the absence of catalysts reactions (iv) and (v) can be neglected because the concentrations of acetylium and acetate ions are insignificantly small. Reactions (ii) and (iii) are assumed to be rapid compared with (i), so that the measured specific reaction rate will be k_1. Associated with it will be an activation energy $E_1 = 20{\cdot}6$ k.cal./mole and entropy of activation, $\triangle S_1^* = -22{\cdot}2$ cal.

The introduction of a catalyst, whether acidic or basic, is assumed to bring about the rapid and total conversion of all the oxalic acid present to the mixed anhydride, oxalyl acetate, so that the mechanism now excludes reaction (i) and the overall rate process can involve only reactions (ii), (iii), (iv) and (v), which can proceed simultaneously. In media of low acetic anhydride content, reaction (iii) will be relatively unimportant. If, in addition the catalyst is present in low concentration, reactions (iv) and (v) will not contribute significantly to the rate, so that the measured specific reaction rate will be k_2. Associated with it will be energy of activation E_2 (about 20·0 k. cal./mole in the case of $HClO_4$ and 20·9 k. cal./mole in the case of H_2SO_4) and entropy of activation $\triangle S_2^*$ (about $-10{\cdot}5$ cal. and $-9{\cdot}4$ cal. for $HClO_4$ and H_2SO_4 catalysis respectively).

If the addition of perchloric acid gives rise to acetylium and of sulphuric acid to acetate ions (see Mackenzie[2]), then, as the catalyst concentration is increased, reaction (iv) in the case of sulphuric acid and reaction (v) in the case of perchloric acid will play a significant part in determining the reaction rate. The measured specific reaction rate will tend, as the concentration of mineral acid is increased, to k_4 or k_5. These would appear from the experimental results to differ only slightly from k_2. Corresponding changes will take place in the energy and entropy of activation, the former tending to E_4 or E_5 and the latter to $\triangle S_4^*$ or $\triangle S_5^*$.

In a medium of high acetic anhydride content, reaction (iii) becomes more important and measured specific reaction rate can approximate to k_3. From Table V it would seem that the corresponding energy of activation, E_3 is about 17 k. cal./mole and the entropy of activation, $\triangle S_3^*$, about -22 cal.

TABLE 1 (30° C)

	20 *per cent v/v* Ac_2O 80 *per cent v/v* $(AcOH)_2$		80 *per cent v/v* Ac_2O 20 *per cent v/v* $(AcOH)_2$	
$^cH_2SO_4$ *mole/litre*	$10^5 j_{-1}$ *sec.*	*Mean*	$10^6 j_{-1}$ *sec.*	*Mean*
0	8·05 (14) 8·15 (20) 8·49 (30) 6·44 (3)	7·78	29·4 (48) 31·5 (53) 31·3 (65) 31·9 (66)	31·0
0·0005	15·7 (36) 14·9 (38)	15·3	92·5 (62)	92·5
0·001	18·7 (35) 18·9 (37) 15·8 (39) 15·5 (4)	17·2	102·6 (51)	103
0·002	19·7 (34)	19·7	—	—
0·01	16·9 (25) 20·9 (28) 20·6 (29) 20·3 (32)	19·7	102·0 (59)	102
0·02	18·5 (10) 20·7 (13) 20·1 (15) 19·9 (24)	19·8	97·4 (57) 99·7 (60)	98·6
0·04	20·4 (23) 22·0 (27) 20·5 (33)	21·0	111·2 (56)	111
0·06	—	—	102·4 (58)	102
0·08	20·9 (22) 20·9 (31)	20·9	112·4 (55)	112
0·1	22·5 (16) 20·6 (17) 20·8 (41)	21·3	114·0 (118)	114
0·12	21·1 (18) 21·0 (21) 23·4 (26)	21·8	—	—
0·3	28·3 (95) 19·1 (108) 22·2 (109) 21·7 (110)	23·0	108·6 (101) 114·1 (105) 92·8 (107)	105
0·5	25·4 (96) 23·9 (99) 23·2 (111) 28·4 (113) 22·4 (115)	24·7	99·0 (100) 121·3 (103) 104·9 (106)	108
0·6	—	—	115·1 (102) 128·5 (104)	122
0·7	24·3 (98) 28·5 (112) 22·8 (116)	25·2	142·0 (117)	142

TABLE I

TABLE II (Various temperatures)

$^cH_2SO_4$ *mole/litre*	° *C.*	20 *per cent v/v* Ac_2O 80 *per cent v/v* $(AcOH)_2$ 10^5j (*sec.* $^{-1}$)	*Mean*	*E* (*k. cal./mole*)	80 *per cent v/v* Ac_2O 20 *per cent v/v* $(AcOH)_2$ 10^5j (*sec.* $^{-1}$)	*Mean*	*E* (*k. cal./mole.*)
0·05	25	10·8 (139)	10·8	20·9	58·3 (140)	58·3	17·0
	30	20·8*	20·8		105*	105	
	35	33·4 (141)	33·4		150 (142)	150	
0·10	22	8·1 (82)	8·2	20·3	49·9 (85)	49·9	17·4
		8·2 (81)			53·3 (84)		
		8·3 (80)			46·4 (83)		
	25	11·8 (79)	11·3		63·7 (86)	64·4	
		11·2 (78)			67·9 (87)		
		10·8 (77)			61·7 (88)		
	30	22·5 (16)	21·3		114·0 (118)	114	
		20·6 (17)					
		20·8 (41)					
	35	33·3 (91)	34·9		158·6 (94)	168	
		35·3 (90)			179·6 (93)		
		36·0 (89)			165·0 (92)		

* Interpolation in Fig. 1.

TABLE III (30°)

$^cHClO_4$ *mole/litre*	$10j^5$ (*sec.*$^{-1}$) 20 *per cent v/v* Ac_2O 80 *per cent v/v* $(AcOH)_2$	80 *per cent v/v* Ac_2O 20 *per cent v/v* $(AcOH)_2$
0·001	16·3 (123)	—
0·005	16·5 (121)	85·9 (129)
0·01	19·6 (122)	—
0·02	22·3 (120)	92·1 (127)
0·05	21·2 (118)	98·2 (125)
0·08	22·0 (124)	—
0·10	21·1 (119)	105 (126)

TABLE IV

c_{HClO_4} *mole/litre*	° *C.*	20 *per cent. v/v* Ac_2O 80 *per cent. v/v* $(AcOH)_2$		80 *per cent. v/v* Ac_2O 20 *per cent. v/v* $(AcOH)_2$	
		$10^5 j$ (*sec.* $^{-1}$)	*E* (*k. cal./mole*)	$10^5 j$ (*sec.* $^{-1}$)	*E* (*k. cal./mole*)
0·05	25	12·0 (135)	20·0	62·0 (136)	16·8
	30	21·2 (118)		98·2 (125)	
	35	34·7 (137)		157 (138)	
0·10	25	12·2 (134)	19·6	70·2 (130)	16·4
	30	21·1 (119)		104 (126)	
	35	36·0 (133)		173 (132)	

TABLE V

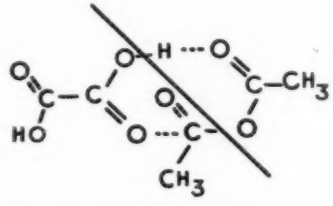
Per cent. v/v Ac_2O:	20		80		
	E (*k. cal. mole.*)	$\triangle S^*$ *at 30° C.* (*cal.*)	*E* (*k. cal./mole.*)	$\triangle S^*$ *at 30° C.* (*cal.*)	*Constant v in the equation* $10^5 j = v(^c Ac_2O + v')$
Uncatalysed	20·6	−22·2	20·6	−22·2	—
0·06 M $HClO_4$	20·0	−10·5	16·8	−22·9	12·3
0·10 M $HClO_4$	19·6	−13·8	16·4	−24·4	
0·05 M H_2SO_4	20·9	− 9·4	17·0	−22·2	13·4
0·10 M H_2SO_4	20·3	−11·4	17·4	−21·0	

TABLE VI (30° C.)

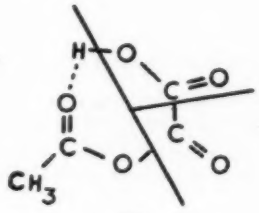
$c_{H_2SO_4}$ *(mole./litre)*	0·001		0·01		0·10	
Per cent v/v Ac_2O	20	80	20	80	20	80
c_{Ac_2O} (mole./litre.)	2·12	8·48	2·12	8·48	2·12	8·48
$10^5 j$ (sec.$^{-1}$) (Mean)	17·2	103	19·7	102	21·3	114
$10^5 j/(13·4\ c_{Ac_2O} - 10)$	0·94	1·00	1·07	1·00	1·16	1·11

Due to the deviation from first order behaviour in the case of pyridine it has not been possible to make any accurate study of energies and entropies of activation, but it is clear that the mechanism must involve some additional feature. Its discovery must await further investigation.

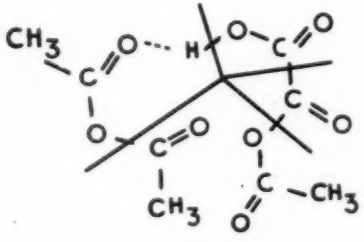
It remains now to examine the plausibility of the mechanism in the light of the measured entropies of activation. According to the above theory the entropies of activation for all the reactions included in the proposed mechanism are negative, but that of reaction (ii) is numerically smaller than the others. The activated complexes characteristic of the transition states for the several reactions are visualized as: (the lines through the formulae indicate how the activated complex can dissociate to give the products):



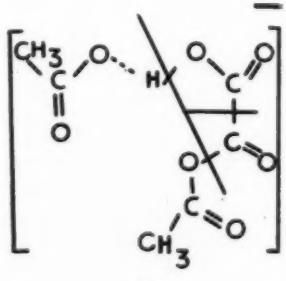
(i)



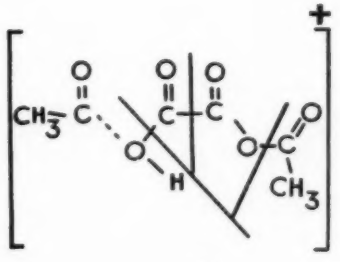
(ii)



(iii)



(iv)



(v)

In all cases except (ii), activation demands the relative orientation of two molecules and therefore a large decrease in thermodynamic probability, so that the change maybe expected to have a large and negative entropy. In reaction (ii), however, the activated

complex arises in the course of rotation within the molecule, so that the transition state is a fairly probable one and the entropy of activation numerically small. In this respect, then the theory is in agreement with the experimental results.

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CHLORINATION TESTS ON SOUTH AFRICAN COALS

by

E. BEYERS AND D. VAN ROOYEN

OPSOMMING

Chloreringstoetse is op fyn gegradeerde steenkool uitgevoer in 'n turbulente laag met gebruik van chloor by lugdruk. Die uitwerking van die reaksietemperatuur en die rang van die steenkool is bestudeer

'n Groot deel van die chloor is herwin in die vorm van soutsuur waarvan die vorming nie vermy kon word nie.

Die gechloreerde steenkool was taamlik stabiel—tot by 300° C. het geen ontbinding plaasgevind nie. Tussen 300° C. en 600° C. is soutsuur afgegee en bokant 600° C. ook chloor. Die gechloreerde steenkool het gedurende karbonisering geen teer afgegee nie. Die produk het in geringe mate met oplossings van alkalië gereageer en donkerkleurige oplossings gevorm.

SUMMARY

Chlorination tests have been conducted on fine, graded coal in a turbulent bed using chlorine at atmospheric pressure. The effect of the reaction temperature and the rank of the coal was studied.

A large proportion of the chlorine was recovered as hydrochloric acid, the formation of which could not be avoided.

The chlorinated coal was fairly stable, no decomposition occurring up to 300° C. From 300° C. to 600° C. hydrochloric acid was evolved and above 600° C. chlorine was also evolved. The chlorinated coal yielded no tar on carbonization. The product reacted to some extent with solutions of alkalies yielding dark coloured solutions.

Comparatively few investigators have studied the reaction of halogens with coal.[1-5] Evidence was found that substitution and addition reactions occur and that more hydrochloric or hydrobromic acid may be formed than could be explained by a substitution reaction. The reaction is exothermic and if the temperature is not controlled the amount of halogen combining with the coal is decreased. Chlorinated or brominated coal was devoid of swelling properties and did not yield tar on carbonization.

Substantial amounts of halogen may combine with the coal, bromine contents of 45·5 per cent[3] and chlorine contents of up to 62 per cent[2] being quoted.

At such high halogen contents the products might have practical value. It was considered, therefore, of interest to determine whether similar products could be prepared from South African coal.

APPARATUS AND EXPERIMENTAL PROCEDURE

The data in the literature suggested that during the chlorination reaction much heat may be liberated and that over-heating may be detrimental. An apparatus was designed, therefore, in which the coal charge could be kept in turbulent motion by a current of chlorine gas. Provision was also made for external cooling or heating of the reaction vessel.

Referring to Fig. 1 the coal was held in the reaction vessel on a sintered glass disc (prepared from glass powder graded $-120 + 170$ mesh B.S.S.). The coal was usually graded $-120 + 200$ mesh B.S.S. and a charge of 10 grams was used.

Chlorine was taken from a bottle fitted with a regulating valve and a by-pass with water seal was provided. The gas rate was determined by means of a flow meter (3 in Fig. 1) and was normally in the region of 150 ml./min. Tests were only conducted at atmospheric pressure.

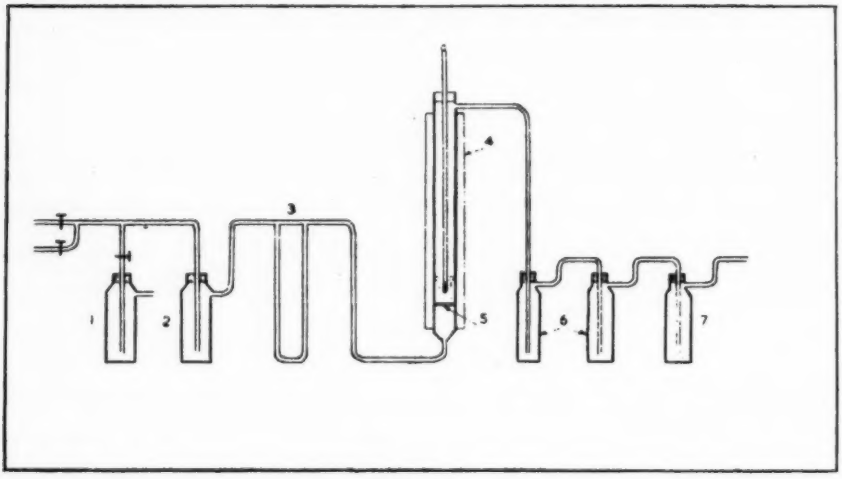


Figure 1.

1. Bypass. 1. Scrubber (H_2SO_4). 3. Flow meter. 4. & 5. Jacketed reaction tube with sintered glass disc (dimensions approximately 1 inch diam. by 12 inches high from sintered glass disc upwards). 6. Gas wash bottles containing distilled water. 7. Scrubber containing alkali.

The gas leaving the reaction vessel was passed through two bubblers containing distilled water to retain hydrochloric acid and finally through a bubbler containing caustic soda solution to absorb excess chlorine. The bubblers with distilled water also retained small quantities of chlorine and this was determined (potassium iodide, thio-sulphate) before determining the hydrochloric acid by direct titration.

In order to determine the rate and extent of chlorination either a series of runs was made, progressively extending the period of chlorination, or samples of coal were removed from the reaction vessel at predetermined intervals for analysis. Before determining the chlorine-content of samples they were placed in a vacuum-desiccator at about 25° C. for at least three hours to remove adsorbed chlorine and hydrochloric acid. The procedure was quite effective as experiments proved that a coal treated at 25° C. lost only a trace of chlorine and about 0·13 per cent. of hydrochloric acid when the temperature of the "coal under vacuum" was raised from 25° C. to 95° C.

For the chlorine determination, samples were mixed with Eschka mixture, ignited and the standard B.S.I. procedure for chlorine followed thereafter.

Reporting results. The amount of chlorine taken up by the coal and the amount of hydrochloric acid evolved, have been expressed as percentages on the original coal.

Coal used. In most of the tests a coal from the Ermelo coalfield having the following average analysis was used:

Ash per cent.	13·9
Moisture per cent.	3·5
Volatile matter per cent.	31·0
Fixed carbon per cent.	51·6

The coal was ground and the size fraction −120 + 200 mesh B.S.S. was generally used.

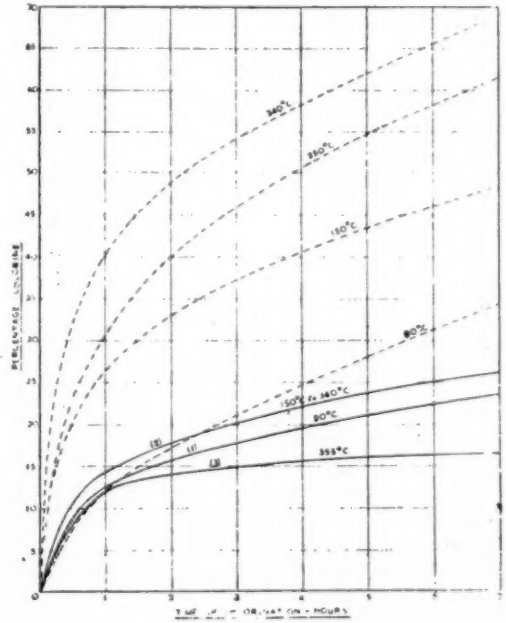
EXPERIMENTAL RESULTS

In the initial experiments the findings of previous investigators could be confirmed that the reaction is exothermic and that the rate of chlorination increases with increasing fineness of the coal.

It was also found that the rate of chlorination increased with the rate at which chlorine was passed through the coal bed (within the limits set by the apparatus), although an excess of chlorine was present at the lowest rate used.

When studying the effect of the temperature of the coal during an experiment, results were obtained which are apparently at variance with those obtained on British coals.[1] It should be borne in mind, however, that those tests were conducted under static conditions while in the present tests a rapid current of chlorine was being passed through the coal.

Tests were conducted over a wide temperature range and results are represented graphically in Fig. 2.



Chlorine absorbed by coal shown thus————
Chlorine evolved as HCl shown thus.....

Figure 2
Effect of temperature on the reaction of chlorine on coal

The results indicate that up to 150° C. the rate of chlorination increases with the temperature. A further rise in temperature to 340° C. did not seem to affect the amount of chlorine retained but at higher temperatures, approaching the decomposition temperature of the

coal, the amount of chlorine retained, decreased appreciably. On the other hand the evolution of hydrochloric acid increased steadily with rising reaction temperatures.

In the light of these experiments it was decided to standardise on a reaction temperature of 150° C. where a reasonably high rate of chlorination could be achieved.

Chlorination of coal to "saturation"

In order to determine how much chlorine the coal would take up, extended tests were conducted. The results obtained in such a test are shown graphically in Fig. 3.

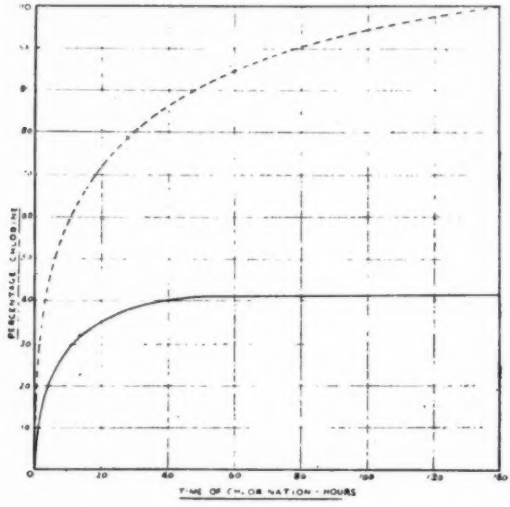


FIGURE 3

Chlorine absorbed by coal shown thus————
Chlorine evolved as HCl shown thus.....

Extensive chlorination of Ermelo coal

It will be noted that the coal reached a saturation point as regards chlorine content after about 50 hours while the evolution of hydrochloric acid persisted even after 140 hours when the experiment was stopped.

The effect of the rank of the coal

In a series of tests typical samples of coal from the Vereeniging, Ermelo (C-Seam) Witbank (No. 2-Seam) and Natal (coking coal) coalfields, were chlorinated under identical conditions. The coals are arranged in order of rank in Table I and it will be noted that there is a general tendency for the rate of chlorination and of evolution of hydrochloric acid to decrease with increasing rank of the coal. In all cases the amount of chlorine converted to hydrochloric acid exceeded that retained by the coal.

TABLE I

Coal charge, 10 grams; Size, −120 + 200 B.S.S.; chlorine velocity, 150 ml./min.; Reaction temp., 150° C.

Period of test (hrs.)	*Per cent. chlorine in solid residue*				*Per cent. chlorine evolved as HCl*			
	Coal				*Coal*			
	Ver.	*Erm.*	*Witb.*	*Natal*	*Ver.*	*Erm.*	*Witb.*	*Natal*
1	23·0	14·5	19·8	8·8	44·7	26·5	33·3	18·2
2	25·6	17·6	23·4	12·1	49·2	32·8	39·2	21·6
3	27·3	20·5	25·7	14·2	53·3	37·2	43·2	24·4
4	28·1	22·3	27·5	15·5	56·3	40·7	46·5	26·9
5	29·0	23·3	29·0	16·6	58·8	43·5	49·2	28·9
6	29·8	24·8	29·9	17·4	60·3	46·1	51·4	30·9
7	30·7	26·4	30·8	18·1	61·3	48·5	53·1	33·0

General characteristics of the reaction and of reaction products

Ultimate analyses of untreated and chlorinated Ermelo coal are given in Table II.

TABLE II

Ultimate analysis of Ermelo coal and of chlorinated coal

Sample	*Moisture (Air dry) (per cent)*	*Wt. reaction prod. g./100 g. of coal*	*Per cent on original coal charged (dry)*						
			C	*O*	*H*	*N*	*S*	*Cl*	*Ash*
Untreated coal	3·8	100	69·5	10·3	4·4	1·7	1·35	—	12·7
Chlorinated 90° C. ...	4·9	160	65·9	13·3	2·6	1·8	1·3	62·4	12·65

Since chlorine interfered with the carbon determination, the C + O figures should be compared rather than the two carbon figures. It will be noted that the hydrogen content decreases. This loss of hydrogen can be accounted for in hydrochloric acid and water formed during the reaction. Not more than traces of volatile organic reaction products could be observed, so that carbon and hydrogen losses from this source may be regarded as negligible.

Concentrated ammonia liquor and sodium carbonate solutions attacked the chlorinated coal to some extent yielding dark coloured solutions. After 24 hours contact with ammonia liquor, 25 to 50 per cent. of the chlorine was removed from the chlorinated coal.

On carbonizing the chlorinated coal no tar was evolved and the "coke residue" was a loose powder.

The chlorine combining with the coal was held quite firmly. After evacuating freshly chlorinated coal (41·8 per cent Cl) at the temperature of the chlorination experiment for 4 hours, the product could be heated to about 300° C. before evidence of appreciable chlorine losses could be observed. The chlorine was liberated as hydrochloric acid (from 300° C.) and chlorine gas (from 600° C.). After heating at 800° C. for 20 minutes the residue still contained 23 per cent. of the chlorine originally present.

This retention of chlorine at 800° C. may be due, in part, to the relatively high mineral matter content of the coal as Eccles and McCulloch[1] have found that chlorinated British coals lost practically all their chlorine by heating them to 500° C.

Action of the chlorine on the mineral constituents of the coal

Further evidence of the action of chlorine on the mineral constituents of the coal was obtained by extracting chlorinated coal with water. Such extracts contained mainly, iron, aluminium and calcium salts.

The progress of the reaction in this respect is illustrated by the results given in Table III.

TABLE III

Iron and aluminium compounds in aqueous extracts of chlorinated coal
Conditions of chlorination: reaction temperature, 150° C.; chlorine rate, 150 ml./min.;
Coal charged, Ermelo coal; Iron and aluminium content of coal (as oxides), 4·07 per cent.

Period of test (hrs.)	*aqueous extract of chlorinated coal contained: (as percent on original coal)*	
	Fe- and Al- oxides	*Total chlorine*
0·5	0·52	2·86
1	0·51	2·71
3	0·50	2·56
5	0·55	2·68
38	0·88	3·23

The results show that only a small percentage of the iron and aluminium compounds appear to be attacked and that this reaction is practically completed in the first half hour of the chlorination.

CONCLUSION

These tests have confirmed that quite high percentages of chlorine can combine with the coal substance, but after the first hour the rate of chlorination is not as high as one would desire under practical conditions.

The most undesirable feature of these experiments was the loss of chlorine by formation of hydrochloric acid. This reaction would have to be depressed to make the reaction at all attractive from a practical point of view. Some exploratory tests in this direction were not successful and at this stage it is rather doubtful whether chlorination could be considered as a possible reaction in the transformation of coal to produce substances of interest to chemical industry.

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Fuel Research Institute of South Africa,
Pretoria.

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CHEMICAL JOURNAL—THE SPECTROGRAPHIC ANALYSIS OF PRINTERS' METALS—

THE SPECTROGRAPHIC ANALYSIS OF PRINTERS' METALS

by

A. STRASHEIM AND T. J. HUGO

OPSOMMING

'n Spektrografiese metode vir die analise van drukkersmetale word beskryf. Die akkuraatheid van die metode is genoegsaam vir die toepassing van die metode in die roetine kwalitetskontrole van drukkersmetale.

SUMMARY

A spectrographic method for the complete analysis of printers' metals is described. The accuracy of the method is sufficiently high for its routine use in quality control.

INTRODUCTION

Chemical composition usually determines the type and quality of printers' metals. These metals consist of the three major elements lead, antimony and tin as well as the minor element copper. Added to these elements nickel, silver, cadmium, bismuth, iron arsenic and zinc are often present as minor element impurities. The concentrations of the major elements for different printers' metals vary as follows: Antimony from 10 per cent to 24 per cent, tin from 3·5 per cent to 12·5 per cent and lead from 65 per cent to 86 per cent. The copper content must not exceed 0·1 per cent. and the total impurity content must be less than 0·1 per cent if the metal is to conform to the specification[1] of the South African Bureau of Standards.

The concentration ranges of the impurity elements are ideally suited to spectrographic methods of analysis but the three major elements have concentrations outside the usual range of this type of analysis. Spectrographic methods[2], [3], [4], however, have been successfully applied to the analysis of elements present in high concentrations. The success of these methods prompted the extension of the method of binary lead-antimony alloys[2] to tertiary lead-antimony-tin alloys. The main requisite of such a method is a high degree of accuracy because it must for instance be capable of distinguishing between 23 per cent. and 23·5 per cent. antimony—a difference of 2·2 per cent. In this contribution a spectrographic method is described capable of giving an accuracy of $\pm$ 2 per cent for the major elements. The method thus provides a means of determining the chemical composition of printers' metals with an accuracy sufficient for quality control except in border-line cases.

Development of the method

A controlled and undamped spark discharge is used for the excitation of the spectrum of the samples. The analytic conditions for the excitation and recording of the spectra are given in Table I.

By means of a series of standard printers' metals analysis curves for antimony and tin using lead as internal standard element were established. The line pairs used were Sb 2692·3/Pb 2697·5 and Sn 2812·6/Pb 2697·5. The measurement of the transmission values of the analysis and internal standard lines was found to be critically dependent on the setting of the focus of the spectral lines on the slit of light-sensitive cell of the microphotometer. The transmission values of the sharp lines Sb 2692·3 and Sn 2812·6 were influenced to a greater degree by improper focus settings than the diffuse internal standard line Pb 2697·5.

TABLE I

Excitation and recording conditions

Light source	An A.R.L. spark generator adjusted to a nominal energy of 2/3 k.v.a. and a primary potential of 70 volts.
Secondary inductance ...	Residual.
Copper electrode ...	A 6 mm. graphite electrode with a hemi-spherical tip.
Lower electrode ...	Sample in the form of a disc.
Electrode separation ...	4·00 mm.
Spectrograph	Hilger, medium quartz, fitted with a constant slit of 0·02 mm.
Pre-spark	10 seconds.
Exposure	20 seconds.
Plate	Ilford thin film half-tone.
Plate processing ...	Developed in 1:1 I.D. 13 for 6 minutes at 18° C. and fixed in F.5
Photometer	A Leeds and Northrup recording microphotometer.

The analysis curves, shown in figure 1, were plotted on log-log paper with the intensity-ratio as the independent and the concentration ratio as the dependent variable. The intensity-ratios were determined as described previously[5] from a plate calibration curve at 2,800 A.

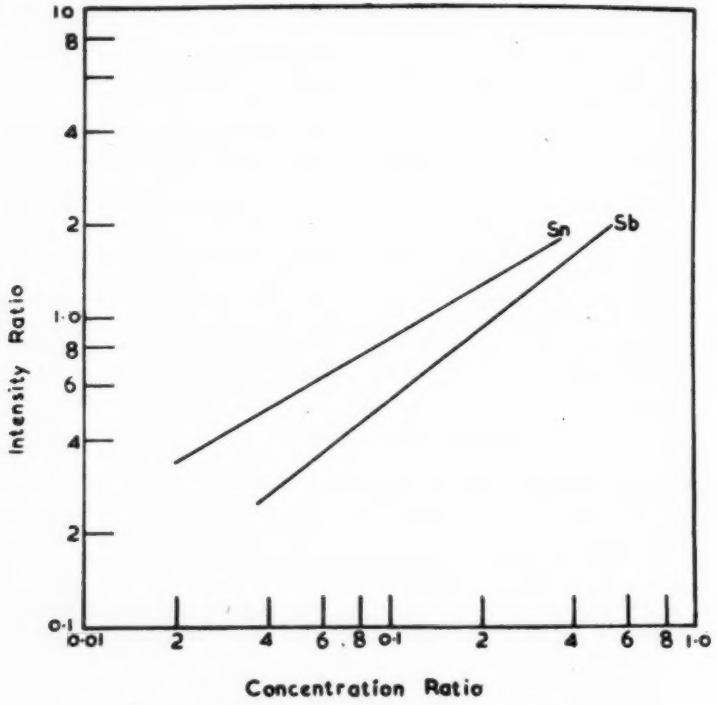

FIG. 1: Analysis curves for antimony and tin.

The line pair Sb 2426·8/Pb 2428·6 which was previously used in combination with the above antimony-lead line pair has to be deleted in the presence of high concentrations of tin due to the masking of the lead line at 2428·6 A by the tin line at 2429·5 A. This interference can be overcome by using a finer slit but the use of the finer slit has an unfavourable influence on the accuracy of the transmission determinations of the spectral lines.

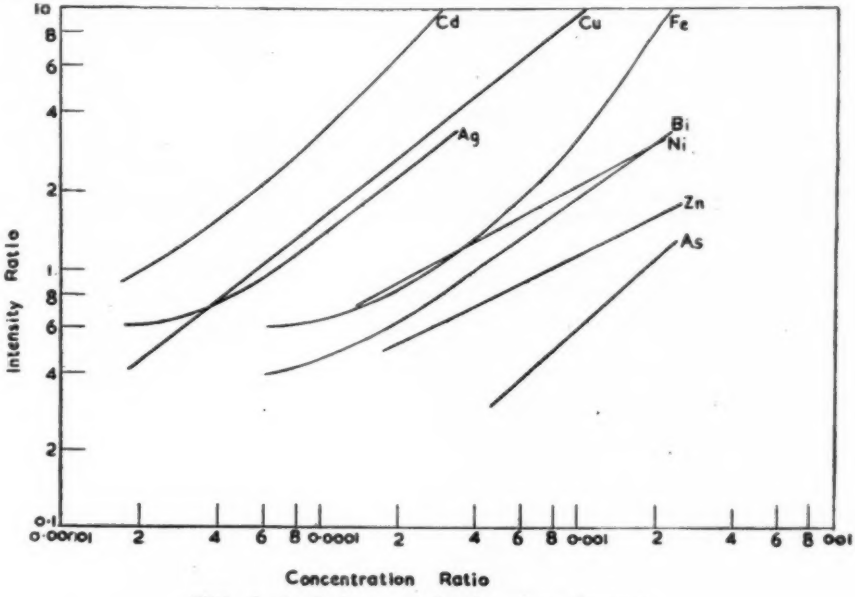

FIG. 2: Analysis curves for the minor elements.

Using the excitation conditions listed in Table I analysis curves for the impurity elements can also be established. The curves shown in Fig. 2 were obtained from two sets of standards, viz., soft solder and soft lead standards. The analysis line pair used as well as the concentration range for each element are shown in Table 2.

TABLE II

Analysis line pairs and concentration ranges for the impurity elements

Element	*Line pair*	*Concentration range in per cent*
Nickel	Ni 3414·8/Pb 3220·5	0·01–0·20
Silver	Ag 3382·9/Pb 3220·5	0·002–0·03
Copper	Cu 3247·5/Pb 3220·5	0·002–0·1
Bismuth	Bi 3067·7/Pb 3220·5	0·005–0·2
Iron	Fe 2739·5/Pb 2697·5	0·005–0·2
Arsenic	As 2349·8/Pb 2332·4	0·01 –0·4
Cadmium	Cd 2265·0/Pb 2332·4	0·002–0·03
Zinc	Zn 2138·6/Pb 2332·4	0·015–0·2

The intensity-ratios for nickel, silver, copper and bismuth were determined from a plate calibration curve at 3220 A, those for arsenic, cadmium and zinc from a curve at 2330 and the ratios for iron from the curve at 2800 A.

The presence of high concentrations of tin in some of the standards did not result in an appreciable shift of the analysis curves except in the case of arsenic where it was found necessary to establish the curve from a set of standards resembling printers' metals.

Analysis technique

Samples are melted and cast according to the technique described previously.[2] In order to overcome the serious difficulty of segregation in the samples it was found necessary to melt and cast the samples at least four times. The samples are cast in a disc form and the spectra excited and photographed under the conditions listed in Table I.

From the analysis curves the concentration ratios R_n for the different elements are obtained. In all cases R_n is given by the equation

$$R_n = \frac{C_n}{C}$$

where C_n = concentration of the n-th element
C = concentration of lead.

If all the concentrations are expressed in percentages the following set of $(n + 1)$ equations is obtained for a complete analysis of the sample:—

$$C_1 + C_2 + --+ C_r + - - - C_n + C = 100 \quad \ldots\ldots\ldots\ldots (1)$$

$$C_r = R_r C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Substituting the values for C_r from equation (2) in (1) the following equation is obtained for the percentage lead in the sample:—

$$C = 100/1 + \Sigma R_r$$

Once the percentage of lead is known the concentrations of the other elements are obtainable from the equations (2). In practice the value of R_r is determined only by the concentration ratios of antimony and tin because the ratios for the minor elements are negligible compared with the values for tin and antimony.

Accuracy of method

A statistical analysis of the results has shown that by doing the analysis in triplicate and spreading the spectra over three plates a reproducibility for the intensity ratios of 1·1 per cent for antimony and 1·4 per cent for tin is obtained. In Table III the spectrographic analysis as well as the chemical values for a batch of samples are shown. In the case of tin a standard deviation of 2·2 per cent from the chemical values is obtained. The corresponding standard deviation for antimony is 2·1 per cent.

TABLE III

Comparison of values obtained by spectrographic and chemical analysis (concentrations are given in per cent.)

Sample No.	*Tin concentrations*		*Antimony concentrations*	
	Spectrographic	*Chemical*	*Spectrographic*	*Chemical*
1	9·4	9·0	13·8	13·7
2	11·0	11·2	22·8	22·4
3	8·7	8·7	19·8	19·0
4	9·1	9·0	14·9	15·0
5	9·5	9·7	14·8	14·7
6	4·0	4·0	11·6	11·4
7	11·2	11·2	14·0	14·0

In Table IV the minor element concentrations for the samples listed in Table III are given.

TABLE IV

Minor element concentrations of printers' metal samples (all concentrations are given in per cent. Concentrations given as XX per cent designate that the elements were not detected and that the concentrations are less than X per cent.)

Sample	*Elements*							
	Cu	*As*	*Zn*	*Bi*	*Ni*	*Fe*	*Ag*	*Cd*
1	0·084	·026	·041	·041	<·015	<·02	·0057	<·002
2	0·002	·040	·021	·010	<·015	<·02	·0061	<·002
3	·011	·047	<·015	·013	<·015	<·02	·0087	<·002
4	.024	.033	.023	.019	<.015	<.02	.0085	<.002
5	.043	·033	.018	.006	<.015	<.02	.0051	<.002
6	·080	·025	·050	·014	<·015	<·02	·006	<·002
7	·066	·033	·033	·014	<·015	<·02	·0068	<·002

The accuracy for the determination of trace elements is about 5 per cent standard deviation at the centre of the analysis range. At the lower limits of the analysis ranges the standard deviation increases sharply and may reach high values especially near the limit of detection. This decrease in accuracy, however, is in most cases, of no practical importance.

The authors wish to thank Mr. T. Fischer of the South African Bureau of Standards for making the chemical analyses and Mr. E. van Deventer for his assistance in the experimental work. This paper is published with the permission of the Council for Scientific and Industrial Research.

National Physical Laboratory,
Council for Scientific and Industrial Research,
Pretoria.

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COLORIMETRIC DETERMINATION OF BORON USING ACETYLATED QUINALIZARIN

by

A. KRUGER

OPSOMMING

'n Kolorimetriese metode vir die bepaling van boor met asetiel-chinalisarien word voorgestel. Metodes vir die bepaling van boor in plante, sowelas die totale en beskikbare boor in grondesoorte word volledig beskrywe. Die ontwikkeling van die bestande metodes word kortliks geskets en die besware teen elkeen word opgenoem.

Die invloed van die volgende veranderlike faktore word aan die hand van afbeeldings verduidelik:— (1) die konsentrasie van die swawelsuur en asynsuur; (2) die invloed van temperatuur op die kleurontwikkeling; (3) die konsentrasie van die reagens en (4) die tyd wat nodig is vir volledige ontwikkeling van die kleur.

Die invloed van steurende stowwe word behandel.

SUMMARY

A colorimetric method for the determination of boron, using acetyl-quinalizarin is proposed. The methods for determination of boron in plant material, total and available boron in soils are described fully. The development of existing methods is explained briefly and their disadvantages indicated.

The effects of the following variables are described with figures (1) The concentration of the sulphuric acid and acetic acid; (2) the concentration of the reagent; (3) the effect of temperature on the development of the colour and (4) the time necessary for complete development.
The influence of interfering substances is discussed.

The evolution of the direct determination of boron started less than 100 years ago. It was stated in 1851 by Rose[1], that up to that time, there had been no direct method for the quantitive determination of boron. Fifty years later a volumetric and gravimetric method were well established, and although complicated and laborious they gave reasonably accurate results for macro-quantities. To-day there are several colorimetric methods for the determination of micro-quantities of boron.

Since a boron deficiency of the beet was described by Brandekorg in 1931[2] interest has been shown in boron as a beneficial fertilizer, and a demand for a specific, accurate and quick method to determine small quantities of boron in plants, soils and water has arisen.

The use of synthetic colours was investigated and in 1930 Feigl[3] reported the colour reaction between boric acid and quinalizarin (1, 2, 5, 8 — tetrahydroxyanthraquinone) in concentrated sulphuric acid, and proposed it as a qualitative test for boron. Since 1935 it has been used extensively for the quantative determination of boron (4–9). The authors of various papers agreed, however, that the concentration of sulphuric acid is very critical and must be between 92–93 per cent in order to obtain satisfactory results. This factor is chiefly responsible for the variations and the unreliable results; thus it has been abandoned in favour of other methods.

Ellis and collaborators[11] tested 60 organic compounds qualitively in concentrated sulphuric acid for their suitability as colorimetric or fluorometric reagents for boron. Finally they selected 1·1[1]-dianthrimide as the best and developed a new method for determining very small amounts of boron. Beer's law is followed and the reaction is sensitive. The sulphuric acid solution of 1·1[1]-dianthrimide and boron test solution, however, must be heated for 5 hours at 80° C. before the colour is completely developed, and the range of this method is short.

None of these methods was entirely satisfactory for the work in hand, as a sensitive method effective over a long range was required. Several other dyes were then examined, but when it was found that the colour reaction between boron and acetyl-quinalizarin appeared to fulfil the requirements, the search was abandoned, and a study was made using this reagent.

The proposed new acetyl-quinalizarin method

When acetic acid or acetic anhydride is added to a sulphuric acid solution of quinalizarin the bluish-violet colour is changed to red, due to the acetylation of part of or all of the OH groups. Upon the addition of boric acid or a borate the red colour is instantly changed to blue. This colour change appears to be due to the formation of an inner complex ester of boronacetic acid according to the description of Dimroth and Faust.[12] This

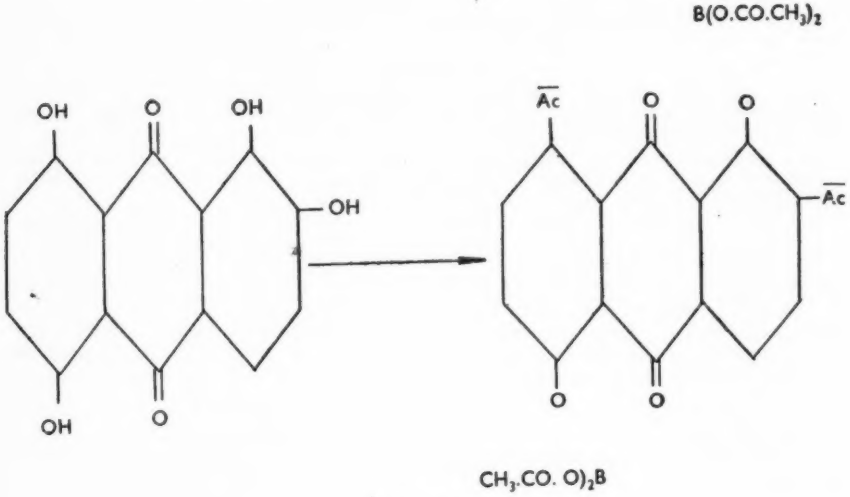

Figure 1
The formation of an inner complex ester of boronacetic acid (16)

colour reaction presents intself as a feasible method for the quantitative determination of boron. It is specific and the concentration of the sulphuric- and acetic acid is not critical, the temperature does not influence the colour and the reaction partly follows Beer's law.

DESCRIPTION OF THE METHOD

Reagents

Acetyl-quinalizarin A. Dissolve 20 mg. quinalizarin in 750 ml. concentrated sulphuric acid and add cautiously 250 ml. glacial acetic acid. Cool and store in tightly stoppered bottles.

Acetyl-quinalizarin B. Dissolve 20 mg. quinalizarin in 550 ml. concentrated sulphuric (c.p.) acid and add cautiously 250 ml. glacial acetic acid and 200 ml. fuming sulphuric acid (15–20 per cent SO_3), shake well and cool. Store in tightly stoppered bottles.

Hydrogen peroxide. "Analar" 90 per cent.

Boron standard. 10 micrograms per ml. Dissolve 0·0571 g. pure dry boric acid in 1 litre distilled water.

Apparatus. A Klett-Summerson photoelectric colorimeter, with an adaptor to take test tubes, was used in this work. Test tubes, to suit the colorimeter, were of Corning alkaline-resistant glass, 20 x 100 mm. In fact Corning alkaline-resistant glass was used entirely.

Procedure A

It has been proved that there is a loss of boron if plant material is ashed, no matter what precautions are taken. The following wet digestion method was preferred:—

Wet digestion. To O·1 g. of finely ground plant material in a Corning alkali-resistant glass test tube, add 2–3 drops hydrogen peroxide and 2 ml. concentrated sulphuric acid. Heat in an oven at 90° C. for half-an-hour, cool and repeat the peroxide and heat treatment until the solution is colourless. The solution must be heated at least half-an-hour after the last addition of hydrogen peroxide, to secure the complete decomposition of the latter. Remove from the oven, cool and add 10 ml. of reagent A. After 30 minutes read in the Klett-Summerson colorimeter against a blank with a filter transmitting in the region of 640 mn.

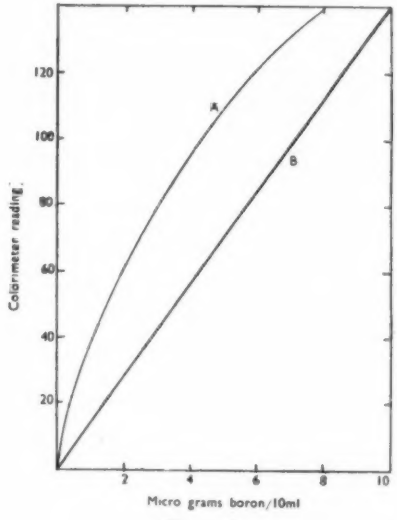

Figure 2.
Calibration curves for boron using the two procedures described.

Standard curve A

Prepare standard tubes containing 0·5 to 10 micrograms boron and 1 ml. saturated calcium hydroxide solution. Dry in an oven at 125° C. and treat exactly as the samples

Available boron in soil. Place 25 g. air-dried, 20 mesh, soil samples in a Corning alkali-resistant boiling flask. Add 50 ml. distilled water and boil "under reflux" for 5 minutes. Cool, add a little calcium hydroxide to facilitate clarification and centrifuge. Take an

aliquot of 10 ml. to dryness in the Corning test tubes at 125° C. in the oven. Add 2 ml. concentrated sulphuric acid and 1 drop hydrogen peroxide, heat in an oven at 90° C. for half-an-hour. Repeat the peroxide treatment if the solution is not clear. Remove from the oven, cool and add 10 ml. reagent. After 30 minutes read in the colorimeter.

Total boron in soil. Fuse 1 g. of soil sample (finely ground) with 6 g. of anhydrous sodium carbonate, and disintegrate the colled mass with 5N. sulphuric acid. The total volume should not exceed 50 ml. (Evaporate further if necessary.) Make up to 250 ml. with alcohol, shake well and leave until the supernatant liquid is clear. Take an aliquot of 10 ml. to dryness in the Corning test tube in an oven at 1,250° C. Add 2 ml. concentrated sulphuric acid and a drop of hydrogen peroxide and heat in an oven at 90° C. for half an hour. Cool and repeat the peroxide treatment if the solution is not clear. Remove from the oven, cool and add 10 ml. reagent A. After 30 minutes read in the colorimeter.

Procedure B

If it is not necessary to destroy organic material and the test sample is in solution, the following procedure may be convenient:

Take 1 ml. aliquot in the Corning test tube and add 10 ml. reagent B. Stir well and allow to stand for 30 minutes. Read in the colorimeter against a blank containing only 1 ml. distilled water and 10 ml. reagent B.

Standard curve B

Prepare standard tubes containing 0·5 to 10 micrograms boron in 1 ml. water. Add 10 ml. reagent B and treat as described before. In all cases it is advisable to do a blank determination.

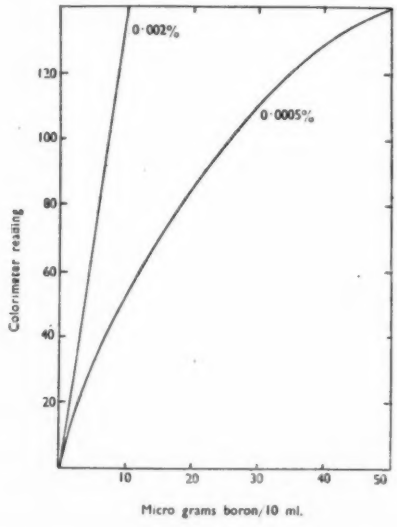

Figure 3
The effect of the concentration of the reagent on the intensity of the colour

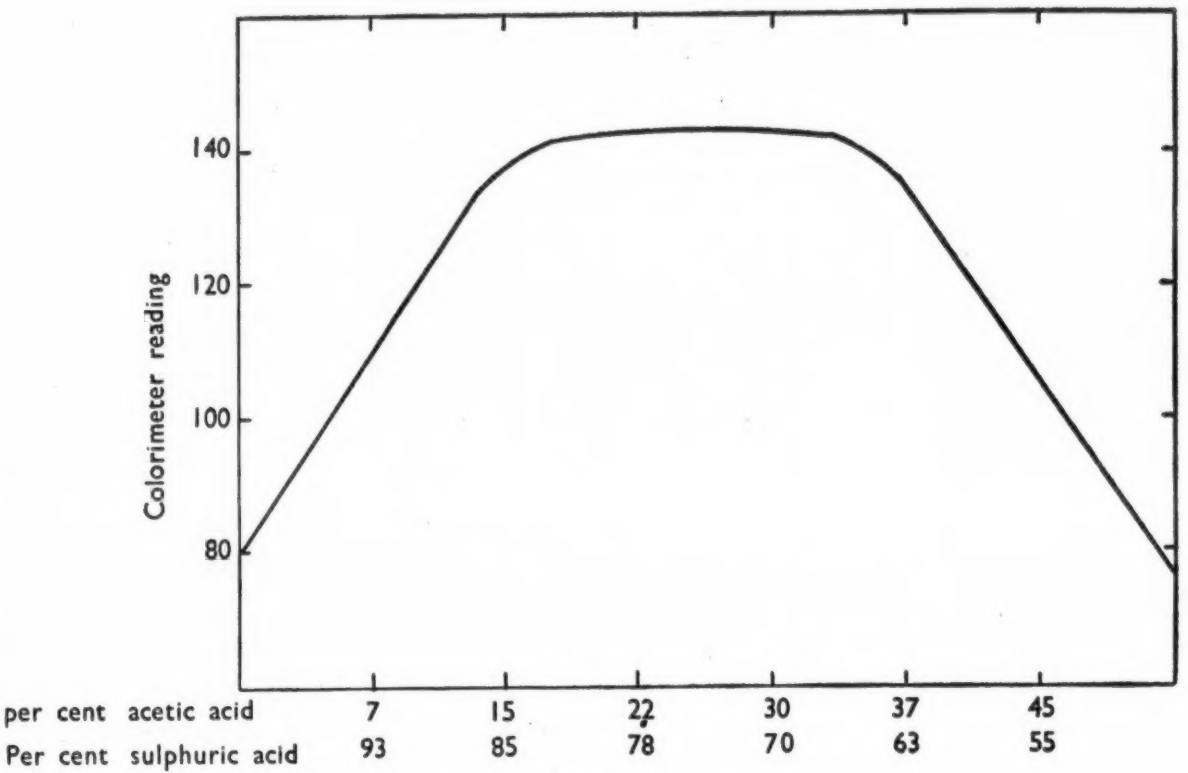

Figure 4.
The effects of the concentration of sulphuric and acetic acid on the intensity of the colour produced

Effect of variables on the colour development

(1) *Interfering substances.* The interference of other elements and groups seems to be the same as that described for quinalizarin. Germanic acid gives a similar colour reaction. Oxidizing agents such as nitrate, ferricyanide and dichromates must be removed before the determination is made.

(2) *The concentration of reagents.* The colour reaction increases in sensitivity if the concentration of the reagent is increased up to about 0·002 per cent. This makes possible an increase in the range, if it is desired. With a concentration of 0·0005 per cent the range may be extended to 30 micrograms boron per 10 ml. Although Beer's law is not followed over the full range, accurate results may thus be obtained.

(3) *The concentration of the sulphuric acid.* The concentration of the sulphuric acid and the acetic acid in the reagent is not critical. A variation from 80 per cent sulphuric acid and 20 per cent acetic acid to 70 per cent sulphuric acid and 30 per cent acetic acid (by volume) makes practically no difference to the results.

The above figure shows the colour intensity given by 5 micrograms boron per 10 ml. reagent with different concentrations of sulphuric acid and acetic acid, but a constant concentration of reagent. It is clear that the sulphuric-acetic acid concentration may safely vary between 80/20 per cent and 70/30 per cent.

(4) *The effect of temperature.* High temperatures had a noticeable effect on the colour intensity. However, with the range ordinary room temperatures there is no significant effect on the intensity of the colour produced.

If the mixture of reagent and boron solution is heated to 60° C. and then cooled to room temperature, the time necessary for maximum colour development is shortened appreciably. Alternating, if the reagent is heated before addition to the boron solution and cooled after mixing, the time necessary for maximum colour development is also shortened.

(5) *Standing time and colour development.* Eighty per cent of the colour developes within the first 5 minutes in both procedures. Procedure A reaches its maximum after standing 40 minutes, whilst Procedure B needs at least one hour. The colour produced by both procedures is stable for at least 24 hours. However, if traces of hydrogen peroxide are still in solution, it is advisable to take the reading as soon as possible.

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S.A. SENECIO ALKALOIDS X—THE STRUCTURES OF SCELERANECIC AND SCELERATINIC ACIDS

by

H. L. DE WAAL, W. J. SERFONTEIN AND C. F. GARBERS

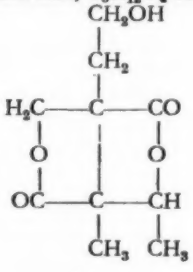
OPSOMMING

Die twee sure wat van natuur in *Senecio Sceleratus* voorkom is sceleranesiensuur en sceleratiensuur, wat alleen van mekaar verskil in sover dat in laasg die primêre hidroksielgroep van eersg deur 'n Cl-atoom verplaas is. Beide sure lewer met oksidasie een en dieselfde afbreeksuur, $C_8H_{12}O_4$, waarvoor 'n hipotetiese formule voorgestel word. Terwyl sceleranesiensuur maklik in sceleratiensuur omgesit kan word, is die teenoorgestelde, naamlik die verplasing van die Cl-atoom deur 'n —OH groep nie moontlik nie. Die rede hiervoor is dat daar by die opening van die laktoongroepe waarskynlik 'n tipe Waldense omkering plaasvind, wat lei tot die vorming van twee nuwe sure nl. 'n dibasiese suur, $C_{10}H_{16}O_6$ Smp. 192° C. (VII) en sy chloorderivaat, $C_{10}H_{15}O_5Cl$ (VIII).

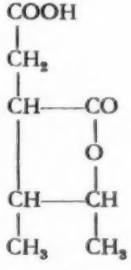
SUMMARY

The two natural acids of *Senecio Sceleratus* are sceleranecic and sceleratinic acids, which only differ from each other in that in the latter the primary hydroxyl of the former is replaced by a Cl-atom. Both acids yield, when oxidized, the same degradation acid, $C_8H_{12}O_4$, for which a hypothetical structure is proposed. Whereas sceleranecic acid can easily be converted into sceleratinic acid, the reverse viz., the replacement of a the Cl-atom by the —OH group could not be affected. The reason for this phenomenon is probably due to a type of Walden's inversion occurring simultaneously with the opening of the lactone groups, resulting in the formation of two new acids, a dibasic acid, $C_{10}H_{16}O_6$, m.p. 192° C (VII) and its chlorine derivative, $C_{10}H_{15}O_5Cl$ (VIII).

In agreement with the experimental and structural data then available, De Waal and Crous[1] in 1948 suggested the following structures for sceleranecic dilactone (I) and its degradation acid, $C_8H_{12}O_4$ of m.p. 100° C.* (II):



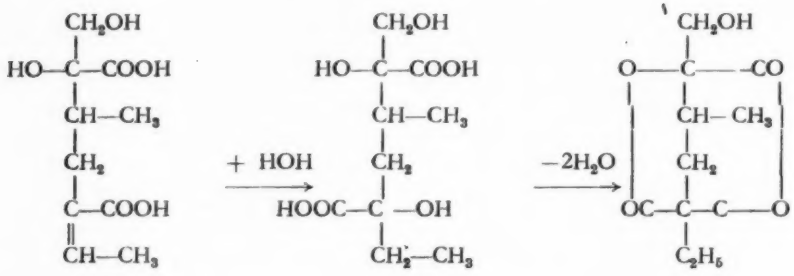
I.



II.

Since then attempts to synthesize the compound (II)[2] failed, perhaps on account of the fact that it contains three asymmetric C-atoms accounting for a number of stereo-isomers and the products crystallized with great difficulty.

In 1949, however, Christie, Kropman, Novellie and Warren[3] assigned the following formula (III) to isatinecic and retronecic acids, which are *cis*- and *trans*-isomers respectively of the same molecular structure. If now water could be made to add on to either acid at the double bond in such a way as to yield (IV), then the latter could lead to the formation of a dilactone (V), which could be identical with the natural sceleranecic dilactone, isolated as such from the plant *Sen. Sceleratus* or obtained upon the hydrolysis of its alkaloid, sceleratine.



III
$C_{10}H_{16}O_6$

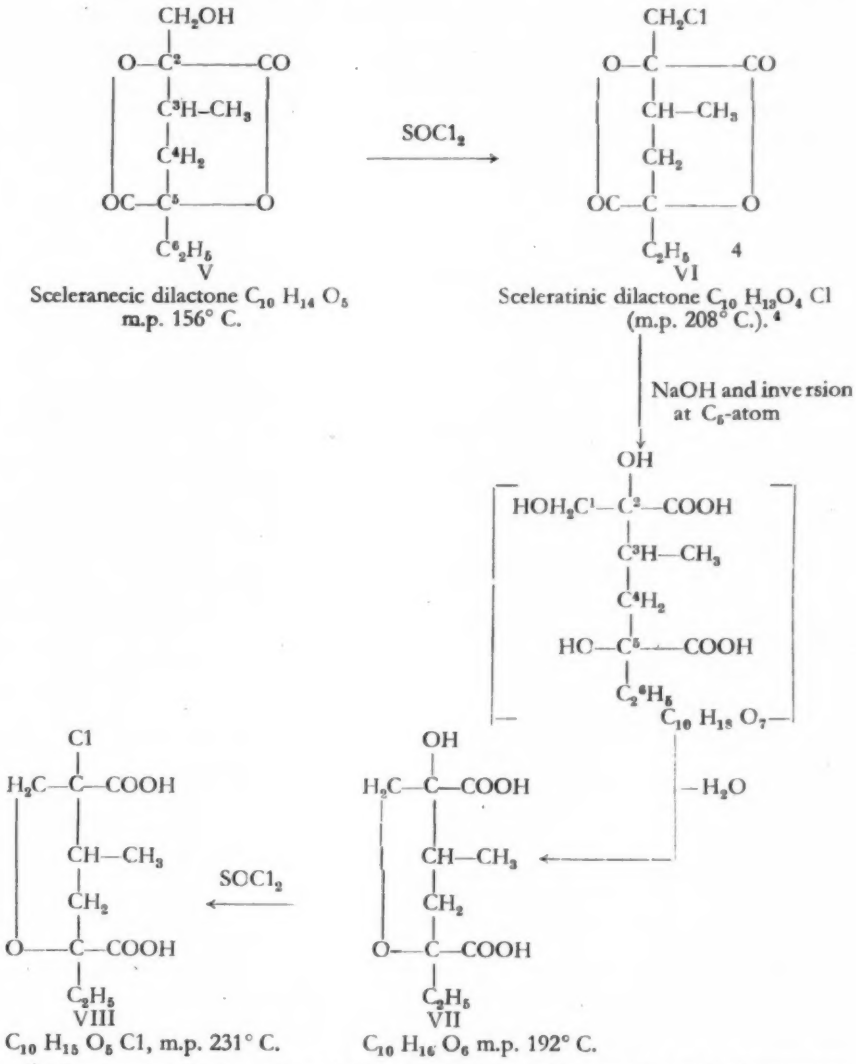
IV
$C_{10}H_{18}O_7$

V
$C_{10}H_{14}O_5$

The chief alkaloids of *Senecio Sceleratus* are isatidine, retrosine and sceleratine, which upon hydrolysis yield isatinecic, retronecic and sceleranecic acids respectively, the latter being only obtainable as its dilactone. One would expect a very close relationship, therefore, among these acids and the above hypothesis of water addition with dilactone formation as in (V) would thus seem feasible for the formation and structure of sceleranecic dilactone as represented by formula (V). Whereas isatinecic and retronecic are both unsaturated dibasic acids, sceleranecic acid is always obtained as its saturated dilactone, whether upon hydrolysis of the alkaloid sceleratine or isolated as such from the same plant. Exhaustive attempts in our laboratory to add on water[4] to isatinecic acid thus to produce after lactonization sceleranecic dilactone failed; instead a saturated dibasic acid $C_{10}H_{16}O_6$ (m.p. 192°) was obtained in a different manner discussed further below. Attempts to replace a hydroxyl group in sceleranecic acid by a halogen atom and then split off a halogen acid to introduce a double bond into the molecule also failed.

Meanwhile de Waal and Louw[5] in a report in 1950, published information relating to the identification of sceleratinic acid (VI) and its relation to sceleranecic acid. Both acids occur freely in *Sen. sceleratus* and the former differs only from the latter in that in sceleratinic dilactone the primary hydroxyl group of sceleranecic dilactone is replaced by a chlorine atom, which had also been proved experimentally[5]. The reverse viz., the replacement of the chlorine atom by the hydroxyl group and the experimental conversion of sceleratinic dilactone to sceleranecic dilactone could not be effected, using either potassium hydroxide, moist silver oxide, or via potassium cyanide followed by moist silver oxide. The reason for this phenomenon is possibly due to a type of Walden's inversion occurring simultaneously at the C_5-atom, resulting in the formation of two new acids, a dibasic acid, m.p. 192°(VIII) $C_{10}H_{16}O_6$, and its chlorine derivative (analogous to VI), viz., $C_{10}H_{15}O_5Cl$ (VIII).

Analysis, titration experiments, etc. confirmed the basicity and molecular formulae of the latter two acids. The completion of a Walden's cycle back to (V) was impossible, on the contrary two new acids (VII) and (VIII) are produced which due to their stable properties especially towards alkali treatment may be ether derivatives. Such an inversion at C_5, once the lactone groupings of sceleranecic and sceleratinic dilactones have been opened, could explain the fact that these two natural plant acids are (*a*) always obtainable only as stable dilactones and (*b*) makes the conversion of sceleratinic acid to sceleranecic thereby impossible. Why silver hydroxide, for example, is not capable of bringing about the latter conversion, however, is not clear.



Sceleranecic dilactone C_{10} H_{14} O_5 m.p. 156° C.

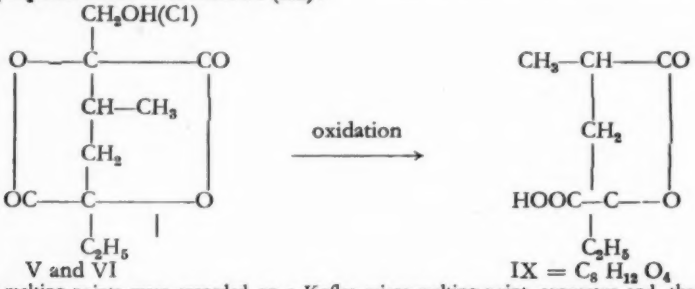
Sceleratinic dilactone C_{10} $H_{13}O_4$ Cl (m.p. 208° C.).[4]

C_{10} H_{15} O_5 Cl, m.p. 231° C.

C_{10} H_{16} O_6 m.p. 192° C.

Both natural acids (i.e., (V) and (VI) when treated with a small excess of potassium hydroxide and oxidized with lead tetra-acetate yield the same degradation acid C_8 H_{12} O_4 m.p. 100° C. This acid again is identical with the C_8 H_{12} O_4 acid obtained by de Waal and Crous[1] when sceleranecic dilactone was oxidized with alkaline potassium permanganate or its primary hydroxyl first oxidized with nitric acid to carboxylic dilactone acid and the

latter then oxidized with chromic acid. These results also confirm the fact that sceleratinic dilactone only differs from sceleranecic dilactone in that in the former chlorine replaced the primary —OH of the latter. Based upon the structure of Warren et al[3] for isatinecic and retronecic acids and assuming formulae (V) and (VI) for sceleranecic and sceleratinic dilactones respectively, therefore, are correct, then the correct formulae for the $C_8H_{12}O_4$ acid must be as follows (IX):



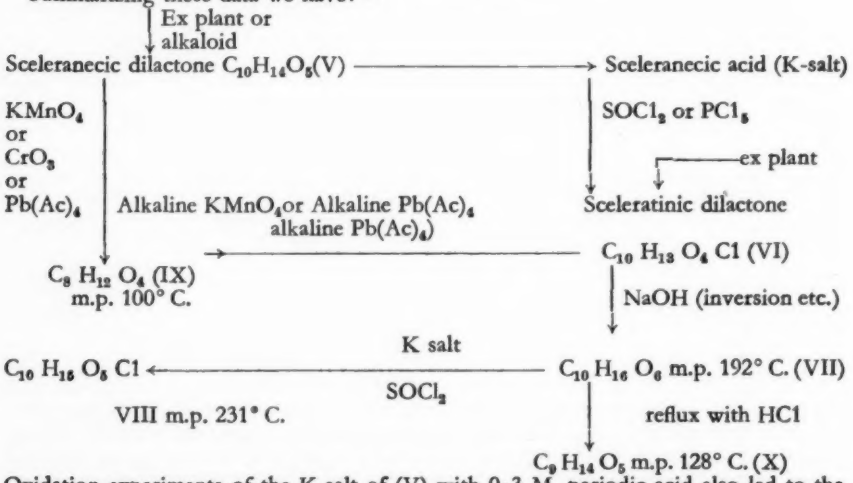
V and VI IX = $C_8H_{12}O_4$

* All melting-points were recorded on a Kofler micro-melting-point apparatus and, therefore, are corrected.

The latter has been proved conclusively to be a monolactonic, monocarboxylic acid

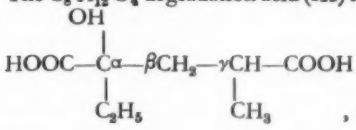
In all of the above oxidations with lead tetra-acetate formaldehyde (accompanied by carbon dioxide) and identified as its 2, 4—dinitrophenylhydrazone derivative, is liberated. The formulation of the reactions for such an oxidation is evident and is a further proof for a glycol-grouping at C_1 and C_2 and a primary hydroxyl group. When the new dibasic acid (VII) is heated with concentrated hydrochloric acid a small yield of another acid $C_9H_{14}O_5$(X), m.p. 128° C., is obtained, also with the liberation of formaldehyde. The Criegee test[6] for a glycol grouping was also positive.

Summarizing these data we have:—



Oxidation experiments of the K-salt of (V) with 0·3 M. periodic acid also led to the formation of formaldehyde, but no crystalline reaction product could be isolated.

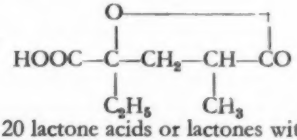
The $C_8H_{12}O_4$ degradation acid (IX) is the lactone of



, which is

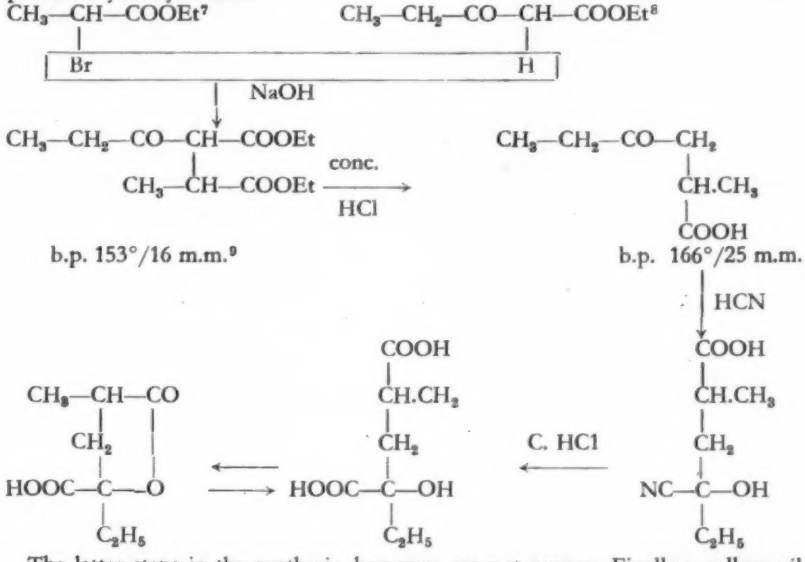
α—hydroxy—α—ethyl—γ—methyl—glutaric acid,

i.e.



, m.p. 100° C.

Over 20 lactone acids or lactones with the molecular formula $C_8H_{12}O_4$ are described in the literature, but a lactone acid with the properties of our acid, m.p. 100° C. is apparently still unknown. An attempt was made to synthesize (IX) according to the following presumably likely scheme:—



The latter steps in the synthesis, however, are not proven. Finally a yellow oil was obtained which effervesced with sodium carbonate solution (carboxyl) and had a spicy odour reminiscent of the acid m.p. 100° C. when still impure, but the synthetic product failed to crystallize. Further work on this synthesis is proceeding.

EXPERIMENTAL

1. Attempts to convert isatinecic acid to sceleranecic acid

(*a*) Treatment of isatinecic acid with 50 per cent sulphuric acid according to H. Stobbe[4] either cold or hot led to the recovery of the unchanged acid.

(*b*) Similarly the treatment of isatinecic acid with hydrobromic acid (Wheland) followed by hydrolysis with sodium hydroxide also did not lead to the addition of the elements of water nor the production of sceleranecic dilactone.

2. Attempts to introduce a double bond into sceleranecic dilactone

The potassium salt of sceleranecic acid was refluxed with thionyl chloride and thereafter treated with potassium hydroxide. The result was (*a*) either the production of sceleratinic dilactone (VI) or (*b*) the formation of the new acid $C_{10}H_{16}O_6$ (m.p. 192° (VII). The failure to introduce a double bond into sceleranecic dilactone indicated the unliklihood that another way of attack in the degradation of this acid could be effected.

3. The preparation of the $C_{10}H_{16}O_6$ acid (VII)

To 0·5 g. sceleratinic acid (dilactone) (VI) a small excess of 2N. potassium hydroxide solution was added and the reaction mixture left for two days at room temperature. It was then acidified with hydrochloric acid using Congo red as indicator, the solution extracted with ether, the combined ether solution dried over calcium chloride and then evaporated in front of a fan. Colourless crystals separated, which were repeatedly recrystallized from ether-petroleum-ether to a constant melting-point of 192° C. The substance effervesced with sodium carbonate solution, was readily soluble in water and ether, but sparingly soluble in chloroform, benzene and petroleum-ether. The substance was a saturated acid containing C, H and O only.

Micro-titration

(i) 24·6 mg. Acid was dissolved in 25 ml. dil. alcohol (1:1H_2O) and titrated with 0·1 N-KOH solution using phenolphthalein as indicator. Two equivalents of alkali (mol. wt. of the acid 232) were used, whether the acid was titrated in the cold, hot or after refluxing for half-an-hour.
23·2 mg. acid (mol. wt. 232) requires 2 ml. O·1 N-KOH for 2—COOH.

(i) Found 24·6 mg. acid used 2·06 ..... 2—COOH.

(ii) Found 10 mg. acid used 2·02 ..... 2—COOH.

Found (i) C, 51·9; H, 7·2.
(ii) C, 51·8; H, 6·7.
$C_{10}H_{16}O_6$ requires: C, 51·77; H, 6·9%.

Decarboxylation experiments with this acid either (*a*) by dry distillation or (*b*) vacuum distillation led to the liberation of carbon dioxide and decomposition.

4. Conversion of $C_{10}H_{16}O_6$ (VII) to $C_9H_{14}O_5$ (X)

When (VII) was evaporated with concentrated hydrochloric acid for a very long period, extending from 10 hours to a week, formaldehyde was liberated while decomposition set in and only a very small yield of $C_9H_{14}O_5$ was obtained. This substance was extracted with ether from the acid mixture, the ether evaporated and a small crop of crystals deposited which was recrystallized from methanol (charcoal) m.p. 128° C. The substance still had acid properties, was easily soluble in water, ether, methanol, ethanol and dioxan and sparingly soluble in benzene, carbon tetrachloride, chloroform and petroleum-ether.

Found: C, 53·15; H, 7·0
C, 53·4 ; H, 7·2.
$C_9H_{14}O_5$ requires: C, 53·5 ; H, 7·0 %.

5. Conversion of $C_{10}H_{16}O_6$ (VII) to $C_{10}H_{18}O_5$ C1 (VIII)

The conversion is similar to that described by de Waal and Louw[6] for sceleranecic dilactone to sceleratinic dilactone. The dry potassium salt of (VII) was treated with thionyl chloride under reflux on a water bath. The excess of thionyl chloride was removed under reduced pressure and a crystalline residue was obtained, which was recrystallized from ether and light petroleum-ether to a substance with a m.p. of 231° C. (Very little of this substance was available so that complete purification was not possible). The substance is fairly soluble in water, soluble in ether and sparingly soluble in petroleum-ether and carbon tetrachloride. The substance was very stable towards alkali.

Found (i): C, 48·0; H, 6·3; Cl, 13·3.
(ii): C, 47·8; H, 6·6; Cl, 13·5.
$C_{10}H_{15}O_5Cl$ requires: C, 47·9; H, 6·0; Cl, 14·1 %.

6 (*a*) Oxydation of sceleranecic dilactone (V) or its potassium salt with lead tetra-acetate [cf. (3), (1D)]

4·6 g. (=0·015 mol.) of the potassium salt of sceleranecic acid was heated with 60 ml. water on a water bath "under reflux". During one hour 14 g. (=0·3 mol.) lead tetra-acetate was added in small successive portions whilst the mixture was well shaken. Reaction with effervescence occurred, formaldehyde was liberated and identified as its 2, 4—dinitrophenylhydrazone, as well as carbon dioxide. After the reaction had ceased an excess of 5 N sulphuric acid was added and the lead sulphate filtered off. The washing from the lead sulphate, were added to the filtrate and the combined solution was dried over calcium chloride concentrated and evaporated in front of a fan at room temperature. When the residue was left in an ice-chest for over a week crystals formed, which were filtered off and recrystallized from carbon tetrachloride – petroleum-ether. The substance was a monocarboxylic monolactonic acid of m.p. 100° C.

(*b*) Oxidation of sceleratinic dilactone (VI) with lead tetra-acetate

Under similar conditions to those described above, the same acid m.p. 100° C. (IX) was obtained from sceleratinic acid with the liberation of formaldehyde as a by-product.

This acid is identical with an authentic specimen prepared from sceleranecic dilactone by the oxidation with alkaline potassium permanganate (cf.[1]). A further analysis and titration experiments confirmed the properties and molecular formula already described for this acid. (Found: C, 55·6 and 55·7; H, 7·2 and 7·1; $C_8H_{12}O_4$: C, 55·8; H, 7·0 %).

A considerable number of lactone acids with this molecular formula are described in the literature, but the above isomer appears to be new and attempts to synthesize it have not yet succeeded.

7. Oxidation experiments with periodic acid[10]

8 ml. O·3 M periodic acid solution was introduced into a flask fitted with a reflux condenser and 2·5 g. of the potassium salt of sceleranecic acid introduced slowly in small fractions while the reaction mixture was kept on a water bath. An energetic reaction occurred with the liberation of formaldehyde. After the reaction was stopped, potassium iodide was filtered off, the filtrate extracted with ether and upon evaporation of the ether a brownish oil was obtained. The oily product would not crystallize but here again presumably the $C_8H_{12}O_4$ (IX) acid had been formed. Previously the latter was only with difficulty crystallizable from carbon tetrachloride-petroleum ether, but fairly pure crystals can readily be obtained by solution in carbon tetrachloride and the gradual addition of light petroleum-ether until a slight turbidity is noticeable.

A melt of sceleranecic dilactone with potassium hydroxide and a little red lead (Pb_3O_4) on a sandbath apparently led to the same result. Further degradation of the C_8 H_{12} O_4 (IX) acid appears to be difficult and it is hoped to present further results of its structure and synthesis at a later date.

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PROPERTIES OF THE BORON HALIDES

PART I. THE VISCOSITY OF BORON TRIFLUORIDE IN THE RANGE 20–200°C.

by

B. A. COOKE AND H. A. E. MACKENZIE

OPSOMMING

Die viskositeit van boortrifluoried is volgens 'n transpirasiemetode bepaal. Sutherland se vergelyking

$$\eta/\eta_0 = \left\{\frac{T_O + C}{T + C}\right\} \cdot (T/To)^{3/2}$$

hou steek met $\eta_o = 156{\cdot}1\ \mu P$ ($To = 273{\cdot}1°K$)
en $C = 194{\cdot}6°\ K$ ($293° K \leq T \leq 476°\ K$).
Die toerie van die metode word ontwikkel.

SUMMARY

The viscosity of boron trifluoride has been measured by a transpiration method. Sutherland's equation

$$\eta_o = \left\{\frac{To + C}{T + C}\right\} \cdot (T/To)^{3/2}$$

is obeyed with $\eta_o = 156{\cdot}1\ \mu P$ ($T_O = 273{\cdot}1°K$)
and $C = 194{\cdot}6°K$ ($293°K \leq T \leq 476°\ K$).
The theory of the method is developed.

APPARATUS AND MEASUREMEMT

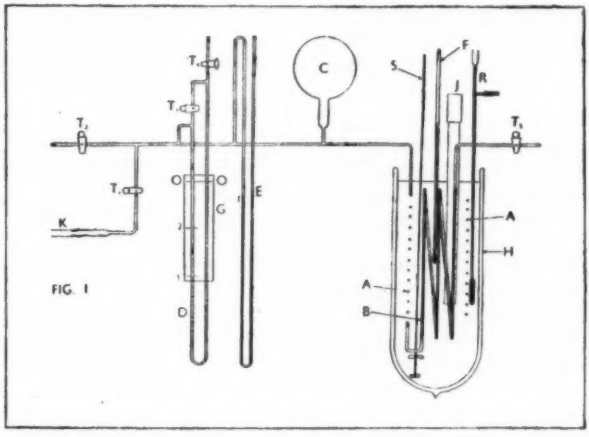


FIG. 1

A sectional view of the apparatus is given in Fig. 1. The procedure was to fill the 1-litre flask, C, to a definite small head above atmospheric pressure by introducing gas at K via the tap, T_1. By opening T_5, with the rest of the system closed, the gas was allowed to leak through the capillary B, and the time required for a definite pressure drop in C was observed. Two manometers were incorporated: E contained mercury and served to measure the pressure in C when the system was evacuated before introducing the gas;

D contained a high boiling paraffin oil, freed from unsaturated compounds which react with boron trifluoride. Alongside D was a scale G with fixed marks 00, 1 and 2. By opening T_3 and closing T_4, D could be "short-circuited" and G adjusted so that the 00 mark coincided with the paraffin level in each arm. When T_3 was closed and T_4 opened, D recorded the pressure head in C; in each determination the time was taken for the paraffin level to rise from 1 to 2. Suitable values for the initial and final pressure heads were found to be 52 and 24 cm. of paraffin respectively. The drop occurred against atmospheric pressure through T_5. The tap, T_2, was used for connecting the apparatus to a high vacuum pump.

The capillary B, was of approximately 0·5 mm. bore and 2m. length and was bent in the form of a rectangular helix. Four metres of 4 mm. tubing, A, was wound round the capillary in the form of a square helix and served as a preheater for the gas. The preheater-capillary arrangement was submerged in water (for temperatures up to 90°C.) or vacuum oil (for temperatures above 90° C.) contained in the large Dewar flask, H. Thermostatic control of the liquid temperature (with a maximum temperature variation of about 0·4 C. at the highest temperatures) was obtained by means of the immersion element, J, and the thermoregulator, R, which operated an electronic relay circuit. A two-bladed propellor stirrer, S, provided efficient mixing of the bath liquid; water was used below 90° C. because of the high viscosity of the oil near room temperature.

Two thermometers were used alternatively at F, the 110° C. instrument being standardized against the $Na_2SO_4 \rightarrow Na_2SO_4 \cdot 10H_2O$ transition point and against steam, while the higher range instrument was calibrated with steam and ethylene glycol vapour. Each thermometer was submerged to a standard point on its scale both in calibration and operation: this eliminated stem exposure errors.

It was found essential to lag the flask, C, and all exposed connecting tubes with cotton wool, so that small variations in ambient temperatures were not transmitted to the apparatus during the short time (2 to 4 minutes) while a determination was being made. The temperature of the gas in C was recorded by a thermometer inserted through the lagging.

THEORY

We must recognize the fact that the whole volume of gas confined between T_1, T_2 and T_5 is not at a single temperature, but the greater part of it, V_o cm.^{3}, is at the temperature T_O, of the inside of the lagging, while a small volume ,V_1 cm.^{3}, equal to the volume of the preheater-capillary arrangement, is at T_1, the temperature of the thermostatic bath. The equations generally given[1] for an apparatus of the transpiration type, therefore, require to be modified. We shall set the argument out in full in order to show that it is not necessary to assume ideality of the gas.

The gases used in the apparatus were air (for standardization) and boron trifluoride. A rough measure of their deviation from ideality can be obtained by regarding them as van der Waals' gases, in which case the fugacity coefficient, f, is given by the relation:

$$\ln f = \frac{p}{RT}\left[b - \frac{a}{RT}\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where a, b are the van der Waals' constants and p and T the pressure and temperature respectively. a and b were estimated from critical data[2] and f computed for a pressure of 0·940 atm. (the average local atmospheric pressure) with the results:

T (° K.)	300	400	500
f (BF_3):	0·9961	0·9982	0·9991
f (air):	0·9993	1·0000	1·0005

Even this rough calculation suffices to show that the fugacity coefficient is never very different from unity within the pressure and temperature ranges of our experimental observations.

The fugacity of a gas, p*, is defined in terms of its chemical potential, μ, by $\mu - \mu^\circ = nRT \ln p^*$, so that

$$pv = p\left(\frac{\delta\mu}{\delta p}\right)_T = nRT\left[1 + \frac{\delta \ln f}{\delta \ln p}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

From (1), we have $\dfrac{\delta \ln f}{\delta \ln p} = \ln f$, and, since $|f-1| << 1$, we obtain, by expanding $\ln f$ and neglecting second and higher powers of $(f-1)$:

$$\left[1 + \frac{\delta \ln f}{\delta \ln p}\right] = f.$$

Therefore, equation (2) can be written:

$$pv = nfRT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Poiseuille's equation for the viscous flow of a gas through a tube of length l and radius a can be written:

$$\delta v = \frac{\pi a^4 \delta p}{8l\eta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where δv is the volume of gas with viscosity η which flows through the tube in one second due to a pressure head, δp. For the present we shall consider an instantaneous bulb pressure, p, and seek an expression for the rate of transpiration of gas between two vessels at constant pressures p and p_o, where p_o in our case is atmospheric pressure. From (3) and (4) we obtain at a particular temperature,

$$p\,\delta v = fRT\,\delta n$$

and

$$\delta n = \frac{\pi a^4}{8RTl\eta} \cdot \frac{p}{f}\,\delta p.$$

For small rates of flow we can write the latter as

$$\frac{dn}{dp} = \frac{\pi a^4}{8RTl\eta} \cdot \frac{p}{f},$$

which gives, on integration between the limits p_o and p,

$$n = \frac{\pi a^4}{16RTl\eta} \cdot \frac{(p^2 - p_o^2)}{f} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$\bar{f}$ is the effective mean fugacity coefficient of the gas which transpires in one second, so that, if dx moles of gas pass through the capillary in dt seconds,

$$\frac{dx}{dt} = \frac{\pi a^4}{16RTl\eta\bar{f}}(p^2 - p_o^2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

dx may be taken to consist of two parts, a contribution from the volume V_o at temperature T_o and a contribution from the volume V_1 at temperature T_1, so that, if the transpiration

of dx moles of gas accompanies a decrease dp in the instantaneous pressure on the high pressure side of the capillary, and bearing in mind the general relation (3):

$$dx = \frac{dp}{R}\left[\frac{V_o}{f_oT_o} + \frac{V_1}{f_1T_1},\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where f_o and f_1 are the fugacity coefficients at T_o and T_1 respectively at the pressure p. Since f_1 occurs only in a small term in (7) and both f_o and f_1 lie close to unity, we have, to a good approximation

$$dx = \frac{dp}{f_oR}\left[\frac{V_oT_1 + V_1T_o}{T_oT_1}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Combining equations (6) and (8) and making use of the facts that f_o and $\bar{f}$ are almost exactly equal and that $T = T_1$, we obtain

$$\frac{dp}{dt} = \frac{\pi a^4(p^2 - p_o^2)\cdot T_o}{16/\eta\ (V_oT_1 + V_1T_o)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Integration gives the time t, for p to fall from p_1 to p_2, thus:

$$\int_{p_1}^{p_2} \frac{dp}{(p^2 - p_o^2)} = \frac{\pi a^4\cdot T_o}{16/\eta\ (V_oT_1 + V_1T_o)} \cdot t, \quad \ldots\ldots\ldots\ldots\ldots(10)$$

and yields an expression for the viscosity of the gas:

$$\eta = \frac{\pi a^4\ p_o\ T_o\ t}{8/\lambda\ (V_oT_1 + V_1T_o)}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

where

$$\lambda = \ln\frac{(p_2 + p_o)\ (p_1 - p_o)}{(p_2 - p_o)\ (p_1 + p_o)}.$$

With the chosen values of p_1 and p_2, variations in the parameter, λ, are quite negligible for the largest observed changes in the atmospheric pressure, p_o, which were of the order of 1 per cent. We may then set $\frac{\pi a^4}{8/\lambda} = k$ and obtain (11) as

$$\eta = \frac{k\ p_o\ T_o\ t}{V_oT + V_1T_o}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

k, which has the dimensions of volume, may be regarded as a constant for the apparatus once p_1 and p_2 have been fixed. Its value may be determined by transpiration experiments on a gas of known viscosity; air was chosen for this purpose.

STANDARDIZATION

The apparatus was evacuated to a pressure of about 0·01 mm. Air was then allowed to leak in slowly through a U-tube containing magnesium perchlorate attached at K. After filling with dry air to atmospheric pressure, the desired pressure head was obtained by displacing air in an aspirator with water. A pause of at least three minutes was allowed for the pressures on the two sides of the capillary to become equal and for the air in the preheater to reach operating temperature. T_5 was then opened and the paraffin level

timed between marks 1 and 2. Readings of atmospheric pressure, bulb temperature and thermostat temperature were also required.

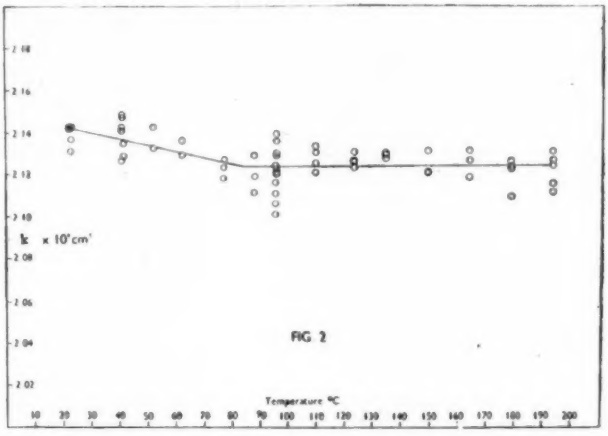


FIG 2

Sutherland's equation was used with $\eta_o = 170{\cdot}9\mu P$ and $C = 114{\cdot}0$ to compute the viscosity data for air.[3] The series of k's determined at different temperatures is shown in Fig. 2. The following empirical relations were found to hold:

$$k = (2{\cdot}148 - 0{\cdot}000287\ \theta) \times 10^{-9}\text{cm.}^3 \quad 20^\circ\text{ C.} < \theta < 84{\cdot}0^\circ\text{ C.} \quad \ldots\ldots\ldots(13)$$

$$k = 2{\cdot}124 \times 10^{-9}\text{cm.}^3 \quad 84{\cdot}0^\circ\text{ C.} < \theta < 200^\circ\text{ C.} \quad \ldots\ldots\ldots\ldots(14)$$

Expression (13) was obtained by the method of least squares from 22 results; statistical analysis showed that there was no significant deviation of the means at each temperature from this linear form; similarly, there was no significant deviation of the means at each temperature above 84° C. from the value $2{\cdot}124 \times 10^{-9}\text{cm.}^3$. All the results were based on estimates of V_o and V_1 as 1055 and 45 cm.^3 respectively. Several of the points below 84° C. were obtained after the higher temperature points had been determined; it was concluded that the unusual form of the standardization curve was not a result of irreproducibility of the measurements with time. As the points were based on temperatures read with carefully standardized thermometers the empirical representation was accepted as standardizing the apparatus.

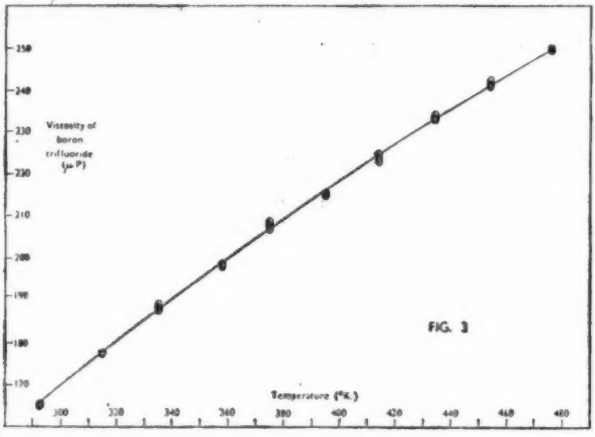
VISCOSITY OF BORON TRIFLUORIDE

The apparatus was evacuated after the taps and ground glass joint had been regreased. A boron trifluoride cylinder[4] was attached to K by means of copper piping and polythene tubing, rubber tubing being avoided. The apparatus was slowly filled and when it was at a pressure slightly above atmospheric, T_3 was closed and T_4 opened.

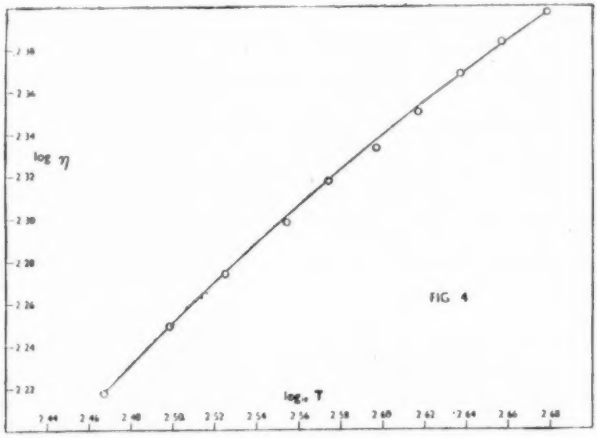
Determinations were made in precisely the same manner as with air. The appropriate value of k was inserted in (12) to obtain η.

A plot of η against temperature is shown in Fig. 3. The curve drawn is an empirical fit by the method of least squares; it is given by the relation

$$\eta \text{ (micropoise)} = -27{\cdot}95 + 0{\cdot}7844T - (4{\cdot}223 \times 10^{-4})T^2 \quad \ldots\ldots\ldots\ldots(15)$$

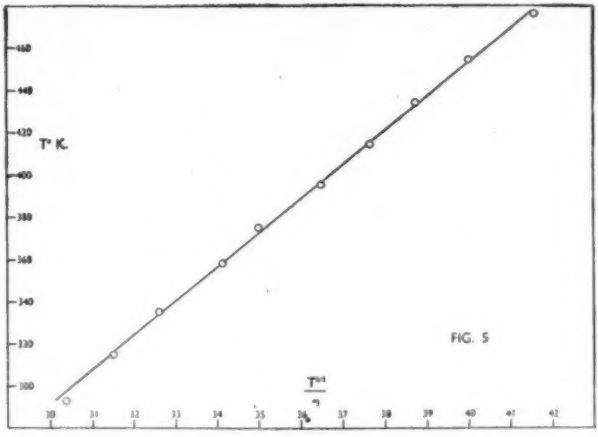


The plot (Fig. 4) of log η against log T shows that if we set $\eta_1/\eta_2 = (T_1/T_2)^n$, n decreases with temperature. In the range 410 to 470° K, n is approximately 0·79 corresponding to a value of ν, the repulsive force index for the inverse power model, of 7·9



Sutherland's equation is obeyed closely. A plot of T against $T^{3/2}/\eta$ is shown in Fig. 5. A fit by the method of least squares gives:

$$T = 16{\cdot}18\,\frac{T^{3/2}}{\eta} - 194{\cdot}6 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$



This is a form of Sutherland's equation,

$$\eta/\eta_o = \left\{\frac{T_o + C}{T + C}\right\} \cdot (T/T_o)^{3/2} \quad ,$$

with C equal to 194·6 and $\eta_o = 156{\cdot}1$ μP (T_o 273·1°K.)

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Alle bydraes moet in triplikaat ingehandig word; indien daar grafieke is moet een stel noukeurig met *Oosindiese ink afgetrek word op gladde wit Bristol-blad of tekenpapier, of op afrolkdoek*—die ander twee stelle kan afdrukke wees, of met potlood geteken word.

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Papers should be as brief as possible compatible with clarity, and no unnecessary experimental details should be included. All papers must be *typewritten in double line spacing*, one one side only of the paper, with a good margin on the left-hand side. The paper should be non-absorbent.

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